Random lasing in Nd:$LuVO_4$ crystal powder

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Abstract: Room temperature random lasing action is demonstrated for the first time in a low concentrated neodymium doped vanadate crystal powder. Laser threshold and emission efficiency are comparable to the ones obtained in stoichiometric borate crystal powders. The present investigation provides a complete picture of the random lasing characteristics of Nd-doped vanadate powder both in the spectral and temporal domain, together with a simplified model which accounts for the most relevant features of the random laser.

OCIS codes: (140.3530) Lasers, Neodymium; (300.6500) Spectroscopy, time-resolved; (160.5690) Rare-earth doped materials.

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1. Introduction

The investigation of lasing action in a large variety of disordered material structures including highly scattering powders, films, colloidal dye solutions, human tissues, etc is a subject of increasing interest [1–3]. In this type of cavityless lasers, multiple light scattering replaces the standard optical cavity of a conventional laser, and the interplay between gain and scattering determines the lasing properties. A detailed discussion about the latest results and theories concerning the mechanisms responsible for random lasing and the precise nature of the random laser modes can be found in Refs [1,4–6].

Since 1986 when Markushev *et al.* demonstrated laser-like behaviour in a powder of $Na_5La_{1-x}Nd_x(MoO_4)_4$ at liquid nitrogen temperature [7], similar random laser experiments have been conducted at room temperature in numerous Nd-doped pulverized materials, mixtures of these powders, and highly scattering Nd-doped ceramics. The history and the state of the art of these neodymium-activated random lasers are reviewed by Noginov in Ref [2]. Among these materials, the stoichiometric $NdAl_3(BO_3)_4$ powder was regarded as a promising room temperature solid-state random laser material [8] because it presents many desirable features, such as a low laser threshold, a high gain, high Nd^{3+} concentration, and excellent physical and chemical properties [9,10]. In a recent paper the authors have studied the random laser performance of ground powders of the yttrium borate family, $Nd_xY_{1-x}Al_3(BO_3)_4$ (x = 0.5-1). In particular, the dependence of their random laser threshold, slope efficiency, and emission kinetics on the Nd^{3+} concentration. Although the obtained results are qualitatively similar in all the explored powders, our findings showed a reduction of the onset of laser-like emission and an increase of the slope efficiency when increasing the Nd^{3+} content [11]. At a first glance this behaviour seems to be unexpected due to the luminescence quenching at high concentrations; however, account taken of the short build up time of the random laser pulses, the lifetime shortening of the excited state, as concentration increases, does not affect the random laser process. It is therefore clear that for a random laser material high effective gain within the build up time scale of the pulse construction is the important issue. Following this idea, the authors have looked for alternative crystal laser materials having higher stimulated emission cross-sections than borates and which could allow using low rare-earth concentration doping but keeping the effective gain still optimal for random laser operation. Among those possible candidates Nd-doped orthovanadate crystals have been proved to be efficient laser materials for diode-pumped solid state lasers due to their large absorption and emission cross sections, high chemical stability, and high damage threshold. Recently Nd^{3+}:$LuVO_4$ has attracted much attention since it was first reported by C. Maunier et al. in 2002 [12]. It has the highest absorption and emission cross-sections among vanadates, $6.9x10^{-19}$ cm^2 at 808 nm and $14.6x10^{-19}$ cm^2 at 1.06 μm respectively. Moreover, the relevance of Nd^{3+}:$LuVO_4$ crystal has been recently confirmed by the demonstration of passively Q-switched laser-diode pumped nanosecond self-Raman laser operating at cascade downconverted frequency [13].

The main drawback of lutetium vanadate crystal is that it is difficult to be grown because of its high melting temperature and the high ion radii differences between neodymium and lutetium [14]. The Nd^{3+} doped lutetium vanadate single crystals used for obtaining the ground powder utilized in the random laser experiments presented in this work were grown by spontaneous nucleation in a $Pb_2V_2O_7$ flux [15]. Reagent-grade PbO and V_2O_5 and 99.99% Lu_2O_3 in the molar ratio 64.7:33.8:1.5 were used as starting materials. The dopant was added as 99.99% Nd_2O_3, and the concentration of Nd^{3+} was nominally 3 mol% with respect to Lu^{3+}.

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A small amount of reagent-grade $Na_2B_4O_7$ was added to produce relatively thick rods [15]. The batch was put in a 50 cm^3 platinum crucible and heated up to 1300 °C inside a horizontal furnace. After a soaking time of 15 h, the temperature was lowered to 900 °C at a rate of 1.8 °C/h. Then the crucible was drawn out from the furnace and quickly inverted to separate the flux from the crystals grown at the bottom of the crucible. This procedure permits fast recovery of most crystals and prevents them from being damaged as a consequence of flux solidification. The flux was then dissolved by use of hot diluted HNO_3. The crystals were grown in the form of clear blue-gray rods elongated in the direction of the *c* crystallographic axis. $LuVO_4$ crystallizes in the zircon structure and belongs to the tetragonal D_{4h}^{19} space group, with lattice parameters a = 7.0254(1) and c = 6.2347(1) Å [16]. The crystal size was approximately 3 × 1 × 0.8 mm^3. The Nd^{3+} concentration in the sample used for random laser experiments was 3 mol%. The crystals were ground to powder of around 3 μm average grain size. The polydispersity of the measured powders were evaluated from SEM (scanning electron microscope) photographs like the one shown in the inset of Fig. 1. The particle size has been computed calculating the mean of the major and minor axis lengths of the grains. As an example Fig. 1 shows the histogram of the particle size. By fitting the histogram to a log-normal function we obtain the average particle size.

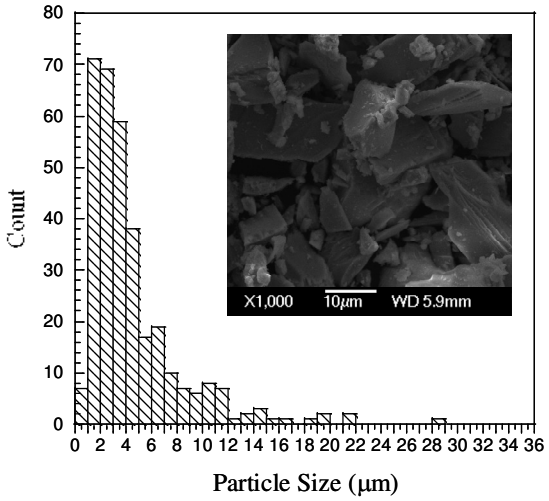

Fig. 1. Histogram of the Nd^{3+}:$LuVO_4$ particle size. The inset shows the SEM photograph of the laser crystal.

It is worth noticing that in spite of the low concentration of neodymium in this vanadate powder, we have obtained a random lasing efficiency at room temperature which is comparable to that found in highly concentrated borates.

The present investigation provides a complete picture both in the spectral and temporal domain of the random lasing characteristics of Nd-doped vanadate powder together with a simplified model which accounts for the most relevant features of the random laser.

2. Laser experiments

The random laser experiments were carried out at room temperature by pumping the Nd^{3+} doped $LuVO_4$ crystal powder with a pulsed Ti-sapphire laser (10 ns pulse duration). The excitation pulse was tuned at the absorption peak wavelength of the $^4I_{9/2} \rightarrow {}^4F_{5/2}$ transition of Nd^{3+} (808 nm). The beam was focused to 3 mm in diameter. We have investigated both emission dynamics and output spectra as a function of pump energy.

The pumping beam energy was controlled by a half-wave plate combined with a polarizer and measured with an energy meter. The emission from the front face of the samples was

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collected in a backscattering arrangement by means of two lenses and a 500 µm diameter optical fiber. The image of the pumped area at the entrance face of the fiber was 1.5 mm diameter, so that only radiation from the central zone of the pumped area was registered. A long-pass filter was used to remove light at the pump wavelength. The spectral measurements of the emitted light were carried out by a TRIAX diode array analyzer (Jobin Yvon-Spex) with a spectral resolution of 0.3 nm and the emission kinetics were recorded by using a fast photodiode (Thorlabs SIR-5) connected to a digital oscilloscope (temporal resolution of 400 ps).

Figure 2 shows the emission spectra of the $^4F_{3/2} \rightarrow ^4I_{11/2}$ transition of Nd^{3+} in the powder sample obtained at low (5 mJ) and high (24 mJ) pumping energies. At low pump energy the spectrum presents the typical spontaneous emission features with a main peak around 1065.6 nm and some additional structures spreading over 10 nm. When increasing the pump energy, there is a threshold value of 9 mJ above which the emission peak intensity suddenly increases whereas the emission spectrum collapses to a narrow single line at 1065.6 nm and 0.3 nm HWHM, our spectral resolution limit.

The emission kinetics parallels the spectral behavior; at low pumping energy the spontaneous emission is single exponential with a decay time of 60 µs whereas above threshold the time profile shortens up and gives a fast emission pulse with a duration of about 800 ps. As pumping increases well above the threshold energy, more pulses appear in the emission temporal profile showing the typical laser relaxation oscillation behavior. As can be seen in Fig. 3, we recorded, at maximum pump energy, up to six oscillations. As is common in conventional solid state lasers, the build-up time (time delay between the output pulses and the pumping pulse) of the random laser pulse decreases gradually as pumping energy increases. As its duration is about 10 ns, this figure clearly shows that the relaxation oscillations remain until the pump pulse is over.

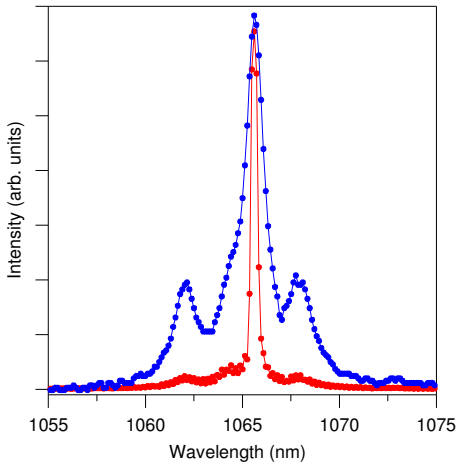

Fig. 2. Normalized emission spectra from Nd^{3+}(3%) $LuVO_4$ powder crystal obtained at pumping energies below (5 mJ blue) and above (24 mJ red) the laser threshold.

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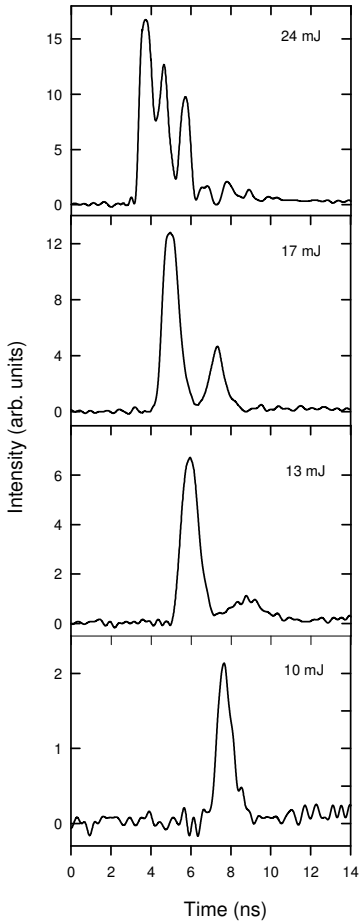

Fig. 3. Stimulated emission intensity pulses of Nd^{3+} (3%): $LuVO_4$ powder crystal as function of time at some different pump energies. The zero time marks the start of the pump pulse.

We have compared the random laser performance of this material with the one obtained in a ground laser powder of $NdAl_3(BO_3)_4$ under the same focusing and measuring conditions. The pumping wavelength used for the borate was 802 nm, which corresponds to its maximal absorption wavelength. To avoid damage in the vanadate sample surface the maximum pump energy used was 25 mJ (about 300 mJ/cm^2). The damage threshold in borate is at least one magnitude order higher.

Figure 4 shows the time integrated intensity of the output pulses from these powders as a function of the pumping energy. The laser threshold was obtained with pump pulses of about 9 mJ for both samples being the slope efficiencies similar but slightly higher for the vanadate sample. The origin of this similar random lasing behaviour relies on the different Nd^{3+} concentrations of both compounds. Although the emission cross section in Nd-doped lutetium vanadate is higher than in the aluminium borate compound, $NdAl_3(BO_3)_4$ is a stoichiometric compound with higher Nd^{3+} concentration (around 20 times) than the 3% Nd^{3+}-doped $LuVO_4$ and therefore it is possible to obtain an "accidental" equalized gain for the random lasing emission. Moreover, although the focussing conditions were the same for both compounds, the pumped volume, and therefore gain, may be different due to the different neodymium concentrations and refractive indices of both compounds. These results therefore suggest that better random laser performances of the vanadate could be achieved with more concentrated powders as has already been demonstrated in Nd-doped borate crystal powders [11].

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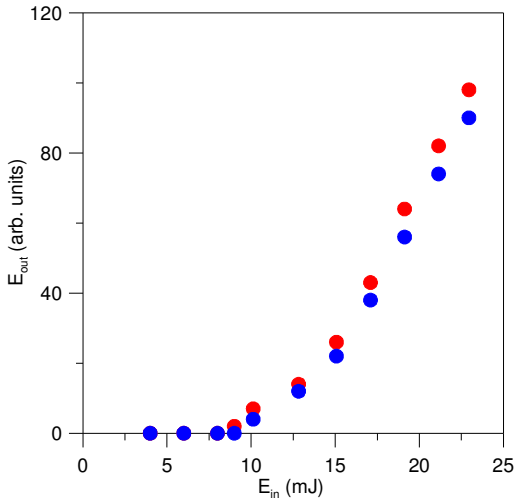

Fig. 4. Laser output energy as a function of the pumping energy for $Nd^{3+}(3\%):LuVO_4$ (red dots) and $NdAl_3(BO_3)_4$ (blue dots) powders.

3. Rate-equation model results

The simplest theoretical models applied to random lasers [10,17,18] are those based on the rate-equations applied to conventional lasers for long, which assume both uniform averaged population inversion and photon density inside the pumped volume. Their application to the present case is adequately described by Eqs. (1-2) displayed below:

$$\frac{dW_0}{dt} = v\sigma_{em}W_0\left(N - N_0\right) + \beta KN \tag{1}$$

$$\frac{dN}{dt} = \frac{I_{in}}{L} - KN - v\sigma_{em}NW_0 \tag{2}$$

where t is the time, N is the population inversion in particles per volume unity, W_0 is the photon density, v is the effective light velocity in the powdered material, σ_{em} the effective stimulated emission cross-section corresponding to the laser transition, accounting for the filling factor, which was calculated by measuring sample volume and weight; K is the total decay-rate from the metastable level, β is the fraction that is added to stimulated emission; in random lasers this parameter is given by the product of the quantum yield and the branching-ratio of the laser level. I_{in} is the pumping effective intensity, i.e. absorbed photons per area and time unity, $L = \sqrt{l_t l_i / 3}$ is the absorption length, estimated from the effective inelastic length l_i, due to pure absorption (with filling factor included) and the transport length in the material l_t due to scattering. Note that L is the thickness of the pumped zone. N_0 is the threshold population inversion, given by $N_0 = \frac{1}{\sigma_{em} l}$, being l the averaged path of the stimulated emission photons inside the material before they leave the sample surface. Therefore, the photon residence time inside the material is given by l/v.

The input values for the numerical calculations performed for the 3% Nd^{3+} doped $LuVO_4$ powder are the following: v = 2x10^8 m/s, σ_{em}=1.46 x10^{-19} cm^2, L has been calculated using a filling factor of 60%, a transport length of l_t = 6 μm, an absorption cross-section of 6.9x10^{-19} cm^2 and a Nd^{3+} concentration of 2.6x10^{20} atoms per cm^3 [19], K=17000 s^{-1} and β = 0.18 [20]. The pump pulse was simulated by the $I_{in}(t)=I_0\ t\ exp(-\alpha\ t)$ function with a time constant α=5x10^8 s^{-1}. The absorption efficiency is difficult to estimate, but account made of the

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absorption and diffusion properties of the material, a value of 25% has been used, mainly due to reflection on the sample [21].

For the $NdAl_3(BO_3)_4$ powder, we have used the following parameter values σ_{em}=1x10^{-18} cm^2, Nd^{3+} concentration = 5x10^{21} atoms per cm^3, absorption cross-section = 6x10^{-20} cm^2, obtained by extrapolation from optical density measurements in samples with low Nd^{3+} concentration. The filling factor was 50%, K=77000 s^{-1}, β = 0.2, l_t = 9 μm [11], being the rest of parameters, the same as those used for the vanadate.

In order to achieve the experimental threshold pumping energies shown in Fig. 4 for both powdered materials, l was used as an adjusting parameter in Eqs. (1-2). The obtained values were l = 130 μm for the vanadate and l = 280 μm for the borate. By using these values and solving Eqs. (1-2) for different pumping energies, we have obtained the same 0.19 slope efficiency for both compounds, which is the absorption efficiency multiplied by the relation between stimulated emission and pumping photon energy.

Although the threshold and slope efficiencies of both samples are well simulated by this simple model, the temporal behavior of the emitted pulses is not so well described. Figure 5(a) shows the temporal shape of the laser output of the vanadate sample predicted by the model whereas Fig. 3 displays the experimental result in this powder at the same pumping energies. Note that the temporal oscillations are much faster in Fig. 5(a) than in Fig. 3. An analogous result was obtained in the borate powder.

To solve this discordance, which also occurs in some other powdered materials [10,17], the model should yield a slower temporal evolution with no changes in the input/output properties of the system (threshold energy and slope) which on the contrary are well reproduced. The direct way to do this is to introduce a minor effective stimulated emission cross section (σ_{em}) and in the same proportion a longer mean path (l) for photons in the material which would affect the temporal behaviour, but as N_0 would not change, threshold and slope would also remain invariant as required.

Figure 5(b) shows the predicted oscillations for l = 1950 μm and an effective stimulated emission cross-section of $\sigma_{em}/15$. After this improvement on the model, quite good predictions of the experimental delay time for lasing, elapsed time among oscillations, and number of oscillations per pulse are attained. On the other hand, strong spatial modal interactions, not considered by this model, are probably the source of the broadening and irregularities of the experimental oscillations, which obviously deteriorate the quality of the comparison.

These results suggest that the zone with high population inversion, given by the absorption length L, is smaller than the zone with a relevant probability of presence of stimulated emission photons. The amplification of the photon is less than expected (lower σ_{em} than nominal value), because a great part of the path it travels is out from the amplifying zone. As a consequence to have an input/output energy and a threshold behavior compatible with the experimental temporal performance of random laser, the length of this travel must be necessarily greater than firstly obtained, which reinforces the idea that the volume of the *effective* laser cavity is greater than the pumped volume [17].

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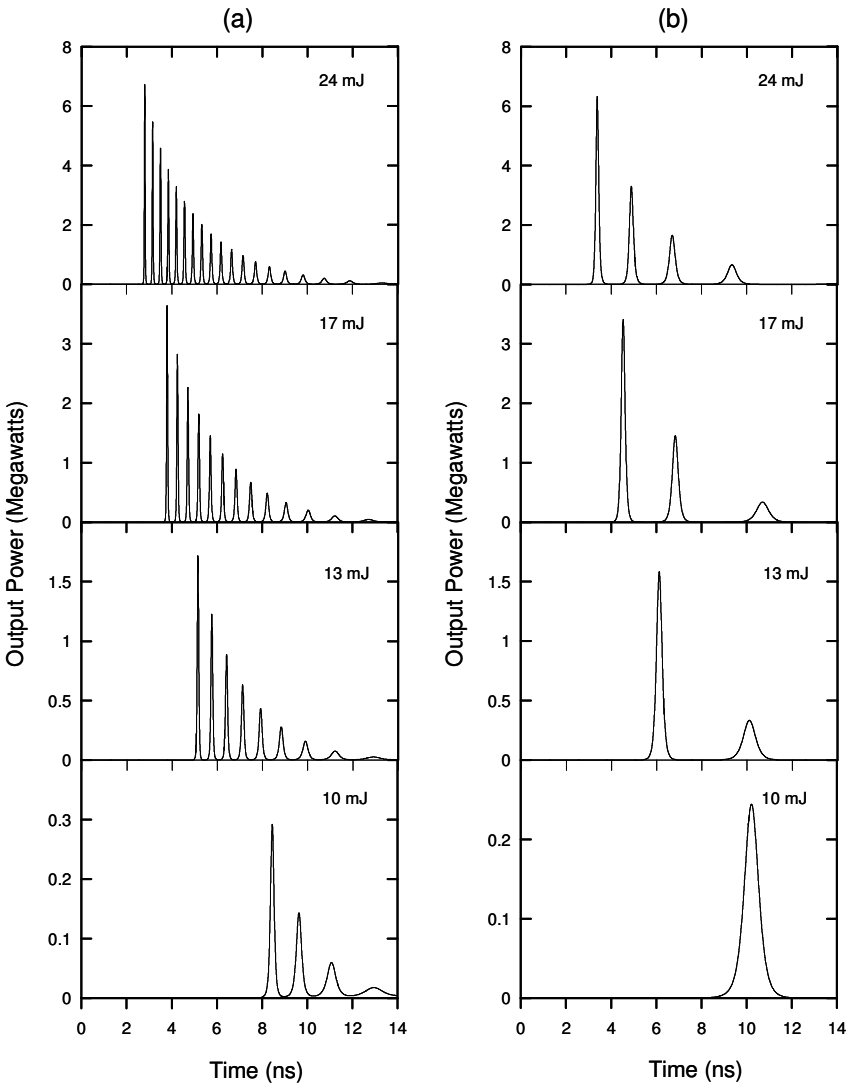

Fig. 5. Theoretical predictions of the laser output of Nd^{3+}(3%):$LuVO_4$ powder crystal as a function of time and for different pumping energies: (a) using l = 130 μm and (b) using l = 1950 μm and σ_{em}/15.

4. Conclusions

We have obtained random laser action from Nd^{3+} doped $LuVO_4$ crystal powder for the first time. We have compared its random laser performance with the one measured, under similar experimental conditions, in the stoichiometric $NdAl_3(BO_3)_4$ crystal powder. Account taken of the similar performance obtained and the very different dopant concentration of both powders, the results open up the possibility of using these Nd-doped vanadates as efficient random laser sources.

We have performed a numerical calculation using rate-equations to obtain the mean free path of the photons generated in both materials before they leave the sample. Although the model predictions are good for the energy threshold and slopes, it cannot describe the temporal behavior of each pulse. In order to improve the predictions of the temporal behavior of the emitted pulses, it is necessary to use minor effective stimulated emission cross-sections σ_{em} as well as longer mean paths l of the photons in these materials by keeping the threshold

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population inversion N_0 constant. As it is suggested in Ref [17], the necessity of these changes must be interpreted on the basis of a larger effective laser cavity volume if compared with the pumped volume.

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