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Two-color random laser based on a Nd^{3+} doped crystalline powder

André L. Moura [a,*], Pablo I.R. Pincheira [b], Lauro J.Q. Maia [c], Anderson S.L. Gomes [b], Cid B. de Araújo [b]

[a] *Grupo de Física da Matéria Condensada, Núcleo de Ciências Exatas – NCEx, Campus Arapiraca, Universidade Federal de Alagoas, 57309-005 Arapiraca, AL, Brazil*
[b] *Departamento de Física, Universidade Federal de Pernambuco, 50670-901 Recife, PE, Brazil*
[c] *Grupo Física de Materiais, Instituto de Física, Universidade Federal de Goiás, 74001-970 Goiânia, GO, Brazil*

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ABSTRACT

Two-color random laser (RL) emission is demonstrated for the first time in a neodymium (Nd^{3+}) doped nanocrystalline powder. Emissions at 1063.5 and 1065.1 nm, due to the Nd^{3+} transition ${}^4F_{3/2} \rightarrow {}^4I_{11/2}$ in $NdAl_3(BO_3)_4$ nanocrystals, were observed by exciting the powder in resonance with the Nd^{3+} transition ${}^4I_{9/2} \rightarrow {}^4F_{5/2}$, at 811 nm. The dual-wavelength emission is attributed to the radiative decay from two nonequivalent site-symmetries occupied by the Nd^{3+} in the $NdAl_3(BO_3)_4$ crystalline structure. The behavior of the Nd^{3+} emissions versus the samples' temperature indicates the possibility of the RL application as a near infrared optical sensor with a large thermal sensitivity of 0.020 °C^{-1}.

1. Introduction

Random lasers (RLs) are based on disordered materials where the multiple scattering of light provides the feedback for laser action. Basically, there are three types of systems already exploited for RLs: one where the scattering particles are embedded in the gain medium [1], e.g., ethanol solution of Rhodamine and TiO_2 particles; a second type that operates via Rayleigh scattering due to inhomogeneities within the glass structure of an optical fiber [2]; and a third type where the particles act as gain medium as well as scatters as in glassy and crystalline powders [3–5]. The low spatial and temporal coherence of the emitted light makes RLs promising to be applied in imaging systems due to the possibility of obtaining speckle-free images with intense illumination sources [6] and several other applications as recently reviewed [7].

RLs based on the neodymium ion (Nd^{3+}) are among the most studied because the 1.06 μm laser emission is interesting for many applications [3,5,6]. The Nd-laser operates as a four-level system where the energy of the lower laser level is $\approx 2000\ cm^{-1}$ above the Nd^{3+} ground state ${}^4I_{9/2}$. Usually, the Nd^{3+} is excited from the ${}^4I_{9/2}$ to the ${}^4F_{5/2}$,${}^4H_{9/2}$ states by light with wavelength around 810 nm; afterwards, the electrons in the ${}^4F_{5/2}$,${}^4H_{9/2}$ states decay mainly to the ${}^4F_{3/2}$ state from where laser action occurs as a transition to the ${}^4I_{11/2}$ state. The RL action occurs when the population inversion between the states ${}^4F_{3/2}$ and ${}^4I_{11/2}$ are large enough to provide gain and it is evidenced by narrowing of the emitted spectrum [3,8,9], an abrupt increasing of the emitted intensity, and shortening of the temporal decay from the ${}^4F_{3/2}$ state as the excitation pulse energy (EPE) is increased beyond certain threshold [3,10]. In some cases relaxation oscillations have also been observed [11,12].

One of the current trends in the RL field is the search for optical effects analogs of the ones observed in conventional lasers (CLs). For example, it was already reported the second-harmonic generation (SHG) in a mixture of $Nd_{0.5}La_{0.5}Al_3(BO_3)_4$ microcrystals and non-centrosymmetric 2-methyl-4-nitroaniline particles [13] that is analogous to the intra-cavity SHG observed for CLs. More recently, it was demonstrated self-frequency conversion of the RL emission at 1062 nm as SHG and sum-frequency generation involving the emission at 1062 nm and the excitation beam at 806 nm in a $Nd_{0.04}Y_{0.96}Al_3(BO_3)_4$ crystalline powder [14]. Also, the operation of RLs based on the stimulated Raman scattering in optical fibers and powders have been reported [2,15,16].

However, the operation of bichromatic RL based on Nd^{3+} was not yet reported. Dual-wavelength lasers (DWL) have been reported for CLs based on bulk crystals doped with Nd^{3+} [17–24] with basis on various mechanisms. The bichromatic emission was due to transitions starting from the Stark levels associated to the ${}^4F_{3/2}$ state [20] and in Ref. [21] emissions at 1064 and 1079 nm were reported for a Nd^{3+}:YAP crystal. Also, since the Nd^{3+} may occupy different sites in the crystalline host [22,23], two laser wavelengths separated by few nanometers were

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[*] Corresponding author.
E-mail address: andre.moura@fis.ufal.br (A.L. Moura).

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observed, at 1059.9 and 1063.8 nm, in a Nd^{3+}:$Y_3Sc_{1.5}Al_{3.5}O_{12}$ ceramic sample [24]. In principle DWL may be exploited for coherent THz generation by nonlinear difference-frequency mixing [19,21,25] that can be used in imaging systems [26].

In this letter we report a bichromatic RL based on sub-micrometer grains of crystalline $NdAl_3(BO_3)_4$ - labeled as NdAB. Previously it was demonstrated RL emission at 1063 nm obtained by excitation of NdAB at 532 nm and $\approx$810 nm, in resonance with the Nd^{3+} transitions $^4I_{9/2} \rightarrow {}^4G_{4/2}$ [11] and $^4I_{9/2} \rightarrow {}^4F_{5/2}, {}^4H_{9/2}$ [27–29], respectively. In the present experiments simultaneous RL emissions at 1063.5 and 1065.1 nm, due to the Nd^{3+} transition $^4F_{3/2} \rightarrow {}^4I_{11/2}$, were obtained by exciting the powder at 811 nm, in resonance with the Nd^{3+} transition $^4I_{9/2} \rightarrow {}^4F_{5/2}$. The RL process was characterized with respect to the emitted spectra, excitation intensity and temperature of the grains. The stability of the system is much larger than in the case of dyes that bleach after hundreds laser shots [30–32].

2. Experimental methods

The NdAB powder was synthesized by the polymeric precursor method using aluminum nitrate nonahydrate ($Al(NO_3)_3 \cdot 9H_2O$), neodymium hexahydrate ($Nd(NO_3)_3 \cdot 6H_2O$), boric acid (H_3BO_3), citric acid ($C_5O_7H_8$) as a complexing agent, and d-sorbitol ($C_6O_6H_{14}$) as polymerizing agent. The synthesis was achieved by dissolving the aluminum and neodymium nitrates in an aqueous solution of citric acid at room temperature. This solution was added to another solution of d-sorbitol and boric acid previously dissolved in water. The obtained solution was annealed at 150 °C in an oven to prompt the polymerization process and to form a dried resin. The molar ratio of citric acid to metals plus boron was 3:1. The citric acid/d-sorbitol mass ratio was set to 3:2. The dried resin was calcinated at 400 °C during 24 h, heat-treated at 700 °C during 24 h and finally annealed at 1150 °C for 5 min under rich-oxygen atmosphere. The powder was characterized using a JEOL JEM 2010 high-resolution transmission electron microscope (HRTEM) operating at 200 keV.

Optical experiments were conducted as in Refs. [10,14] with the powder gently pressed into a sample-holder. The excitation source was an Optical Parametric Oscillator (OPO) pumped by the second-harmonic of a Q-switched Nd:YAG laser (7 ns, 10 Hz). The laser repetition rate was low to prevent heating of the grains. The light beam from the OPO was focused on the sample by a 10 cm focal length lens and the illuminated area was 1.2 mm^2. The excitation wavelength, with full width at half maximum of $\sim$1.0 nm, was tuned around 811 nm to be in resonance with the Nd^{3+} transition $^4I_{9/2} \rightarrow {}^4F_{5/2}$. The EPE was controlled by a pair of polarizers and measured with a calibrated photodiode. The angle between the normal to the sample and the incident laser beam was 35° and the scattered light was collected from the front surface of the sample. Optical filters were used to eliminate the excitation laser residue from the collected signal. To change the powder's temperature, the sample-holder was placed on a hot-plate from where the emitted light was collected with a 5 cm focal length lens, focused inside of an optical fiber and sent to a spectrometer equipped with a cooled CCD (resolution: 0.024 nm). The powder temperature was determined by a thermocouple fitted in the sample holder. Unless specified, the measurements were performed at room temperature of 22 °C.

3. Results and discussion

Images of the particles are presented in Fig. 1(a) and (b) and the particles' size histogram, shown in Fig. 1(c), was obtained by measuring 110 particles with most particles having dimension of $\sim$55 nm. The crystalline $NdAl_3(BO_3)_4$ particles present well defined structural planes, and Fig. 1(b) shows that the powder is composed of non-spherical particles of irregular forms.

The RL emission was characterized by recording the emitted spectra of the Nd^{3+} transition $^4F_{3/2} \rightarrow {}^4I_{11/2}$ and monitoring the emitted light intensity versus the EPE. Fig. 2(a), (b) and (c) shows the behavior for EPE corresponding to 0.2, 0.3, and 1.6 mJ, respectively. The insets of Fig. 2(b) and (c) show the Nd^{3+} energy levels diagram with the transitions corresponding to the excitation at 811 nm and the emissions around 1.06 μm. Two narrow emissions at 1063.5 and 1065.1 nm were unveiled as the EPE was increased.

The intensity dependence of the Nd^{3+} emissions versus the EPE is shown in Fig. 3(a) where the RL action is revealed by the change in the slope efficiencies for the emissions at 1063.5 and 1065.1 nm. For $0.30\ mJ < EPE < 0.54\ mJ$ only the emission at 1063.5 nm was observed. Another evidence of RL emission is the spectral narrowing that is noticeable by comparing Fig. 2(a) and (b). The RL emission was also corroborated by the reduction of the lifetime, τ, of the $^4F_{3/2}$ state, e.g. for $EPE < 0.30$ mJ we measured $\tau \approx 50\ \mu s$ while for $EPE > 0.30$ mJ it was measured to be $\tau \approx 10$ ns.

The emissions at 1063.5 and 1065.1 nm are attributed to the Nd^{3+} positioned in two different crystalline sites labeled A and B, indicated in the inset of Fig. 2(c). The existence of nonequivalent Nd^{3+} environments in the $NdAl_3(BO_3)_4$ crystal was reported in Ref. [33]. It was demonstrated that the ions in different sites feel different crystalline fields that correspond to different absorption and emission spectra. Depending on the number of sites, it is possible to have multiline laser oscillation, as already reported in conventional lasers [34], and the laser spectrum can be strongly dependent on the excitation wavelength due to different absorption spectra of the Nd^{3+} located in the different sites. In a similar manner, the RL spectrum reported in the present manuscript was dependent on the excitation wavelength as follows. For excitation at 810 nm, only the RL emission at 1063.5 nm was observed with the peculiarity that the slope efficiency was larger than that obtained by exciting at 811 nm. For excitation wavelength beyond 811 nm, the intensities of both emissions decreased compared to

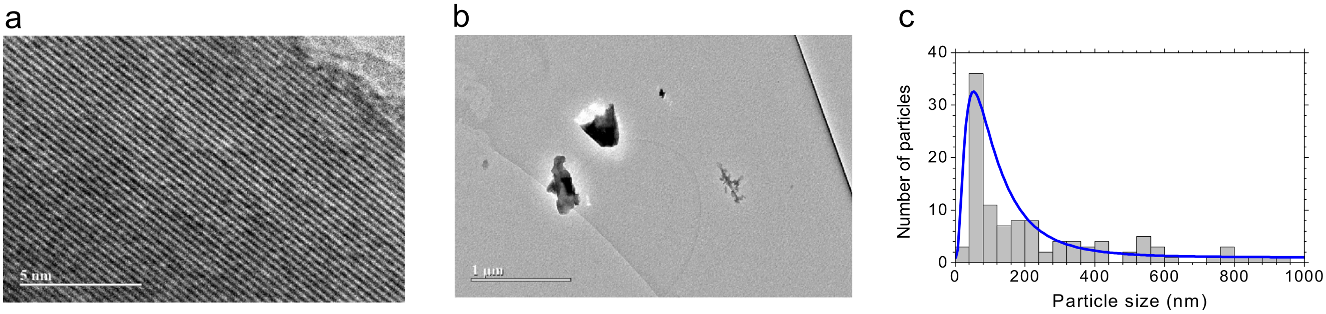

Fig. 1. (a) TEM, (b) HRTEM images, and (c) particle size histogram of the $NdAl_3(BO_3)_4$ powder.