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Spectral properties of Pr:CNGG crystals grown by micro-pulling-down method*

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Pr^{3+}-doped calcium niobium gallium garnet (Pr:CNGG) single crystals with different Pr^{3+}concentrations are successfully grown by the micro-pulling-down (μ-PD) method. The crystal structure, room-temperature absorption spectra, and fluorescence spectra of Pr:CNGG crystals are measured and discussed. The fluorescence results indicate their large dependence on the doping concentration. The fluorescence lifetime of the $^1D_2$ energy level is also determined. The results indicate that Pr:CNGG crystal could be a potential solid-state laser gain medium.

Keywords: Pr:CNGG, μ-PD method, spectral properties

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1. Introduction

The trivalent praseodymium ion (Pr^{3+}) has been widely studied in the past few years due to the rich emission spectrum in ultraviolet, visible, and infrared regions.[1–3] The first Pr-based laser output was achieved in $CaWO_4$ crystal, operating at 1.047 μm.[4] After that, blue light emission was realized in Pr:$LiYF_4$ crystal by using a pulsed dye laser.[5] With the development of GaN/InGaN laser diodes (LDs), the research process of the Pr^{3+}-doped materials has been promoted. So far, Pr^{3+}-doped hosts, such as crystals[6–8] and glasses,[9] have been widely investigated.

The CNGG crystal belongs to the cubic phase (Ia3d) garnet-type structure, which is the representative disordered crystal. It is characterized by low melting point (about 1460 ℃) in comparison with other garnet crystals, and excellent mechanical and thermal properties in comparison with glasses.[10] In addition, the random distribution of Nb^{5+}, Ga^{3+} and cationic vacancies in the host lattices cause the spectra of the doped rare-earth ions to significantly inhomogeneously broaden,[11] which makes it possible to produce ultra-short pulses. Up to now, a large number of research focuses on rare ion-doped CNGG crystals.[12–15] Nevertheless, only one paper reported the crystal growth and structural properties of Pr:CNGG crystal,[16] but the spectral properties were not mentioned in detail, to the best of our knowledge.

The μ-PD method allows the direct growing of fiber-shaped single crystals with a diameter as low as 300 μm, and it has many advantages over the conventional crystal growth methods, such as fast growth rate, low cost, and controllable crystal shape. So the μ-PD method is a promising method of growing gain media for miniature lasers.

In this paper, we grow the Pr:CNGG single crystals by the μ-PD method. The crystal structure, room-temperature spectral properties and lifetimes of Pr:CNGG crystals are measured and discussed in detail.

2. Experimental details

2.1. Crystal growth

The CNGG single crystals doped with 0.5, 1.0, and 2.0 at.% Pr^{3+} were successfully grown by the μ-PD method. The $CaCO_3$, Nb_2O_5, Ga_2O_3, and Pr_6O_{11} powders with a purity of 99.999% were prepared as starting materials and weighted according to the formula $Ca_3Nb_{1.6875}Ga_{3.1875}O_{12}$. The Pr_6O_{11} powders were doped together with additional Ga_2O_3 in a ratio of 3:5 (mol%) to form $Pr_3Ga_5O_{12}$.[17] Pr-doping as a garnet phase is important to maintain garnet composition in melt. The powders were well mixed and pressed into bulks, then sintered at 1300 ℃ for 12 h in a muffle furnace with air atmosphere in order to react completely. The polycrystalline material was melted within a platinum crucible, and then passed through the micro-nozzle at the bottom of the crucible with a pulling rate of 0.5 mm/min. The growth direction was along the ⟨111⟩ orientation. The as-grown Pr:CNGG single crystals with an

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average diameter of about 2 mm is shown in Fig. 1. The crystals were transparent and had a little yellow color, changing from light to deep with the increase of Pr^{3+} concentration.

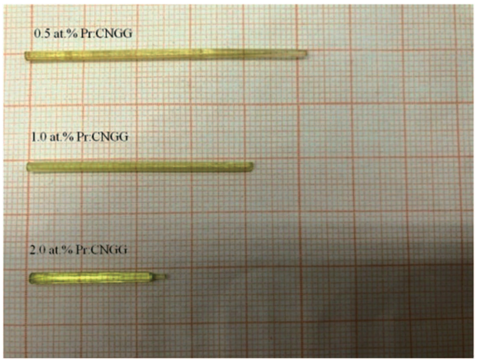


Fig. 1. As-grown Pr:CNGG single crystals.

2.2. Characterizations

To identify the structure of the grown Pr:CNGG crystals, the x-ray diffraction (XRD) analysis was carried out in the 2θ ranging from 10° to 90° using an automated Ultima IV diffractometer (Cu target, Kα, Rigaku, Japan) with a scan width of 0.014° at room temperature. Samples with a thickness of 1.07 mm were cut perpendicularly to the growth orientation $\langle 111 \rangle$ and their faces were optically polished for the spectroscopic measurements. The absorption spectra with a resolution of 1 nm were measured from 400 nm to 2500 nm by a spectrophotometer (Cary5000, UV-VIS-IR). The fluorescence spectra and decay curves of the crystals were obtained by an FLS980 fluorescence spectrometer (Edinburgh Company, England). The exciting source was a xenon lamp. All the measurements were carried out at room temperature.

3. Results and discussion

3.1. XRD pattern

The samples are cut from the as-grown crystals and grounded into powder for XRD measurement. Figure 2 shows the XRD patterns of Pr:CNGG crystals. The diffraction peak positions and relative intensity of samples are in good agreement with those of the undoped CNGG crystal and ICSD Card No. 261821,[18] and no other phase is found in the lattice structure after Pr^{3+} ions have been doped into CNGG crystals, which implies that the Pr:CNGG crystals have the same crystallographic structure as pure CNGG crystal and belong to the cubic phase (Ia3d) garnet-type structure.

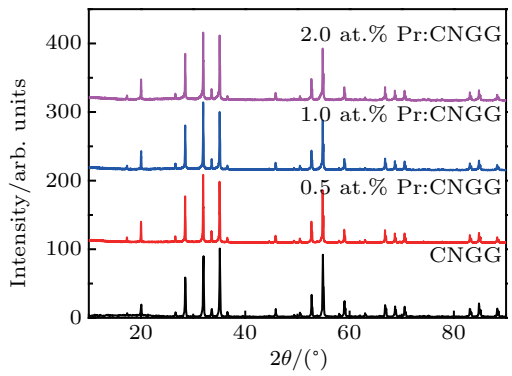


Fig. 2. XRD patterns of Pr:CNGG crystals.

3.2. Spectral properties

Figure 3 shows the absorption spectra of the Pr:CNGG crystals with different dopant concentrations in the range of 420 nm–620 nm and 1200 nm–2500 nm. The absorption spectra consist of seven prominent absorption bands, which correspond to the transitions from ground state $^3H_4$ to excited states $^3P_2$, $^3P_1+{}^1I_6$, $^3P_0$, $^1D_2$, $^3F_3+{}^3F_4$, $^3F_2$, and $^3H_6$, respectively. The absorption coefficients of 0.5, 1.0, and 2.0 at.% Pr:CNGG crystals at 449 nm are 1.26 cm^{-1}, 2.88 cm^{-1}, and 4.80 cm^{-1}, respectively. The full widths at half-maximum (FWHMs) of the absorption peak at 449 nm for different concentrations are similar, which is about 7 nm. The full width at half-maximum (FWHM) of Pr:CNGG crystal is larger than that of Pr:$LiLuF_4$ (1.7 nm),[19] Pr:$LiYF_4$ (1.8 nm),[19] and Pr:LaF_3 (5 nm),[20] which makes Pr:CNGG crystal more suitable to be pumped by the GaN/InGaN LD.

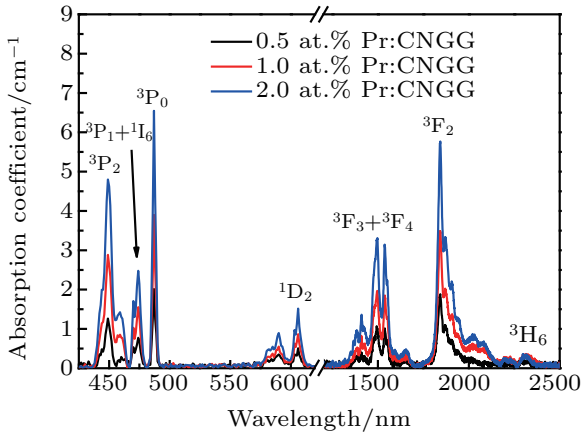


Fig. 3. Absorption spectra of Pr:CNGG crystals.

The fluorescence spectra of the Pr:CNGG crystals in the visible range under excitation at 449 nm and in the near-infrared (NIR) range under excitation at 606 nm are presented in Fig. 4. The emission bands in the visible range mainly correspond to the transition from $^3P_0$ and $^1D_2$ energy level to lower levels. In the NIR range, there are two intensive fluorescence bands centered at 824 nm and 1082 nm, corresponding to the transitions from excited state $^1D_2$ to $^3H_6+{}^3F_2$ and $^3F_3+{}^3F_4$, respectively.

Obvious differences could be found when the doping concentration of Pr^{3+} increases from 0.5 at.% to 2.0 at.%. Firstly, 0.5-at.% Pr:CNGG crystal shows a larger fluorescence ratio of $^1D_2 \rightarrow {}^3H_4$ and $^1D_2 \rightarrow {}^3H_5$ transition centered at 606 nm and 632 nm than other Pr:CNGG crystals with higher Pr^{3+} concentration. There are two kinds of cross relaxation processes between Pr^{3+} ions[21] in Pr:CNGG crystal as shown in

Fig. 5. The populations accumulate on the $^1D_2$ energy level by the multi-phonon relaxation from $^3P_0$ energy level and the cross relaxation between $^3P_0 \rightarrow {}^1D_2$ and $^3H_4 \rightarrow {}^3H_6$ (CR1). As the Pr^{3+} concentration increases, the cross relaxation between $^1D_2 \rightarrow {}^1G_4$ and $^3H_4 \rightarrow {}^3F_4$ (CR2) increases, resulting in the fluorescence quenching of $^1D_2$ energy level. Thus, 0.5-at.% Pr:CNGG crystal shows relatively large fluorescence ratio of emission bands centered 606 nm and 632 nm, derived from the transition of $^1D_2$ energy level. The result of multi-phonon relaxation and CR1 is that the fluorescence intensity centered at 617 nm, corresponding to the transition from $^3P_0$ to $^3H_6$, is very weak. The most intensive fluorescence band of 2.0-at.% Pr:CNGG crystal is centered at 654 nm in the red spectral region.A similar phenomenon has been reported in Pr^{3+}-doped phosphate glasses.[21] Secondly, 1.0-at.% and 2.0-at.% Pr:CNGG crystals show similar fluorescence ratios in the NIR range. The FWHMs of the fluorescence bands centered at 606 nm and 654 nm are both about 7 nm, which are larger than that of Pr:$LiLuF_4$, Pr:$LiYF_4$,[19] and Pr:$YAlO_3$.[22] The FWHM of the emission band centered at 1082 nm is about 41 nm, indicating that a tunable and ultrafast laser around 1082 nm may be realized in Pr:CNGG crystal.

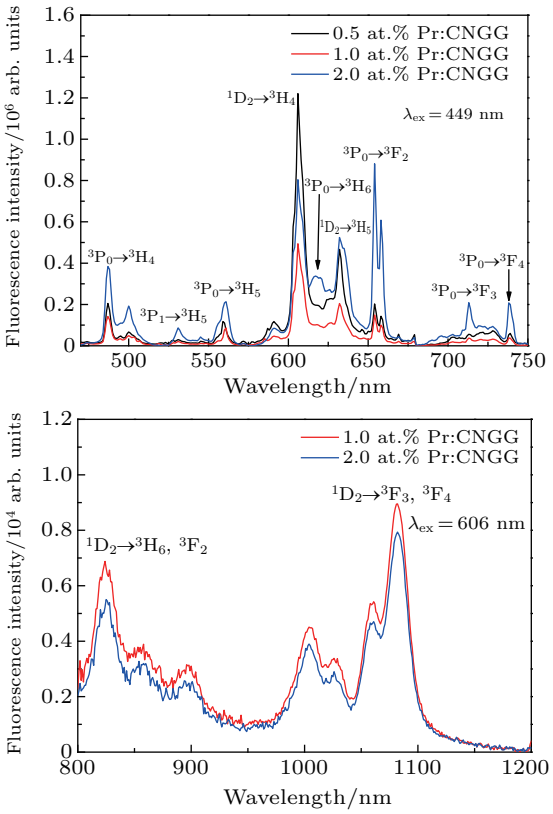


Fig. 4. Fluorescence spectra of the Pr:CNGG crystals in the visible and NIR range.

The fluorescence decay curves at 606 nm corresponding to the $^1D_2$ energy level, under excitation at 449 nm are shown in Fig. 6. The fluorescence lifetime of the $^1D_2$ energy level in the 0.5, 1.0, and 2.0-at.% Pr:CNGG crystals are estimated at 47.52 μs, 37.63 μs, and 26.24 μs, which are smaller than that of 0.5% Pr:YAG (110 μs),[23] 1% Pr:GGG (118 μs),[24] but larger than that of 1% Pr:YAP (28 μs).[25] The fluorescence lifetime decreases from 47.52 μs to 26.24 μs when the doping concentration of Pr^{3+} increases from 0.5 at.% to 2.0 at.%, which is mainly due to the depopulation of the $^1D_2$ level, caused by CR2 as shown in Fig. 5 and concentration quenching effect.[26,27]

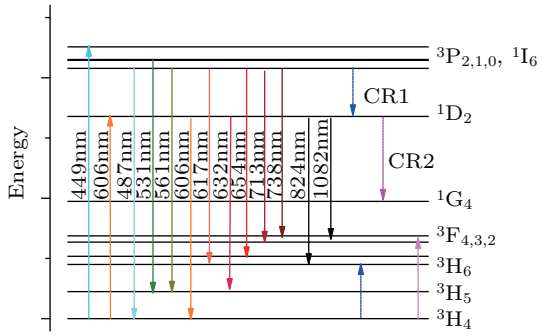


Fig. 5. Simple diagram of energy configuration of Pr^{3+} in CNGG crystal and cross relaxation processes.

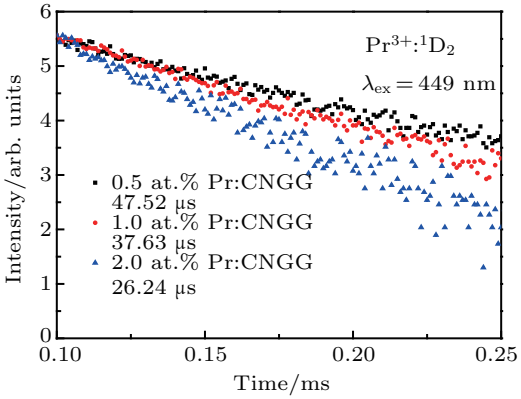


Fig. 6. Intensity decaying with time of $^1D_2$ energy level of Pr:CNGG crystals.

4. Conclusions

The CNGG crystals doped with 0.5-, 1.0-, and 2.0-at.% Pr^{3+} ions are successfully grown by the μ-PD method. The doping of Pr^{3+} does not influence the lattice structure of CNGG. The spectral properties are studied at room temperature. The Pr:CNGG crystals have higher absorption coefficient and broader absorption band width at 449 nm, which are suitable for LD pumping. For the 0.5-at.% Pr:CNGG crystal, the orange emission band at 606 nm is more marked while the most intensive fluorescence band of 2.0-at.% Pr:CNGG crystal is centered at 654 nm in the red spectral region. In the NIR range, 1.0-at.% and 2.0-at.% Pr:CNGG crystals exhibit similar fluorescence ratios. The room temperature fluorescence lifetimes of $^1D_2$ energy level are fitted to be 47.52 μs, 37.63 μs, and 26.24 μs for 0.5-, 1.0-, and 2.0-at.% Pr:CNGG crystals, respectively. Results of this work demonstrate that Pr:CNGG crystal owes good spectral properties and may be a potential candidate for solid-state laser operation.

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