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Spectroscopic properties of $Nd:Gd_{0.89}La_{0.1}NbO_4$ mixed laser crystal

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ABSTRACT

A Nd-doped niobate mixed laser crystal of $Nd_{0.01}:Gd_{0.89}La_{0.1}NbO_4$ (Nd:GLNO) has been grown successfully by Czochralski method. The absorption spectrum, fluorescence spectrum and fluorescence decay curve of Nd:GLNO crystal were measured at room temperature. The spectral parameters of Nd:GLNO crystal were obtained based on Judd-Ofelt (J-O) theory calculation. The three intensity parameters $\Omega_{t(t=2,\ 4,\ 6)}$ were calculated to be 6.61, 1.43 and 3.31×10^{-20} cm^2, respectively. On the base of the Ω_t calculation, the branching ratios, spontaneous radiative probabilities, radiative lifetime and fluorescence quantum efficiency of the $^4F_{3/2}$ level have been evaluated. Compared with other Nd-doped niobate laser crystal, Nd:GLNO shows a special spectral properties due to the large structure disorder caused by La^{3+}. All the results demonstrate that this crystal is a specific low symmetrical laser material different from other niobates family crystals such as $Nd:GdNbO_4$ (Nd:GNO) and $Nd:YNbO_4$ (Nd:YNO) and can be considered as a promising laser material suitable for laser diode pumping.

1. Introduction

Since the first ruby crystal laser was reported in 1960 [1], laser crystals have undergone development for nearly 60 years. Recently, with the rapid development of high power laser diodes, much attention have been paid on the investigation of new Nd-doped materials that have good diode-pumped laser properties [2–4], because Nd-doped crystals are highly desirable for the bright applications in optical communication, medical treatment, environmental instrumentation measurements and scientific research [5–7]. Among all of the traditional Nd-doped laser crystals, Nd:YAG and Nd-doped vanadates family crystal (including $Nd:YVO_4$, $Nd:GdVO_4$, mixed vanadate crystals and so on) attract most of the attentions and have achieved fruitful research results [8–10]. However, the absorption bandwidth of Nd:YAG at around 808 nm is extremely narrow, indicating that it shows a strong sensitivity to the pumping wavelength. And the biggest obstacle for the Nd-doped vanadate family crystals is the component volatility during its growth process, resulting in difficulty to grow high-quality and large-size single crystals [11].

Nowadays, tantalate and niobate crystal with the general formula $ReMO_4$ (Re = Y or Gd and M = Ta or Nb) have been grown successfully with Czochralski method and reported as attractive candidates of laser host materials for solid state lasers [11–13]. A maximum continue-wave (CW) laser output of 2.5 W and 1.1 W corresponding to slope efficiency of 36% and 35.3% have been achieved with Nd: $GdTaO_4$ and $Nd:GdNbO_4$ crystal, respectively. Moreover, Nd-doped tantalate and niobate mixed crystal, represent by $Nd:GdYTaO_4$ (Nd:GYTO) and $Nd:GdYNbO_4$ (Nd:GYNO) [14,15], also have attracted the attention from researchers because the Nd^{3+} experience a disordered crystal field in the mixed crystal, resulting in inhomogeneous broadening of the absorption and luminescence spectra. The broadened absorption bands can efficient improves the pumping efficiency and the increased luminescence linewidth is beneficial to generate short laser pulse [16]. A maximum CW laser output of 2.37 W and 0.98 W corresponding to slope efficiency of 38% and 30.4% have been achieved with Nd:GYTO and Nd:GYNO crystal, respectively. However, up to now, mixed tantalate and niobate crystal with La-doped is rarely reported. That is because La is the first one in lanthanide series with the largest ions diameter, thus, the mixed crystal with La-doped will possess a higher disorder structure and very easily to crack, resulting in it difficult to grown by Cz method [17]. However, it is very worthy to investigate La-doped mixed crystal due to the higher disorder structure and broader spectral linewidth.

Fortunately, after many time tries, a Nd-doped $GdLaNbO_4$ (Nd:GLNO) crystal with high crystalline quality was obtained by Cz method. The absorption spectra, fluorescence spectra as well as fluorescence decay curves of Nd:GLNO crystal were presented in this work. The spectral parameters were calculated based on Judd–Ofelt (J–O)

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Fig. 1. Photograph of the as-grown Nd:GLNO laser crystal.

theory calculation.

2. Experiments

A Nd:GLNO crystal with chemical formula of $Nd_{0.01}$:$Gd_{0.89}La_{0.1}NbO_4$ was grown by the conventional Cz method in an iridium crucible, with N_2 as protective atmosphere. Nd_2O_3 (99.999%), Gd_2O_3 (99.999%), La_2O_3 (99.99%) and Nb_2O_5 (99.99%) were used as raw materials. A *a*-orientated $GdNbO_4$ crystal was used as seed crystal. Then, a Nd:GLNO crystal with dimensions of $\Phi 28 \times 25\,mm^3$ was obtained, as shown in Fig. 1. The as-grown crystal was annealed in air atmosphere at 1450 °C for 48 h in order to eliminate the residual stress.

The crystal structure of Nd:GLNO crystal was measured using a Philips X′pert PRO X-ray powder diffractometer equipped with Cu Kα radiation. The diffraction peaks were recorded in the 2θ range of $10^{\circ} - 90^{\circ}$ with a scan step rate of $0.02^{\circ}\,min^{-1}$. The absorption spectra of Nd:GLNO crystal in the wavelength range of 320–950 nm were recorded by PE lambda 950 spectrophotometer with spectral interval of 1 nm. An Edinburgh FLSP-920 spectrophotometer was employed to record the photoluminescence spectra and the fluorescence decay curves with the excitation source of a continuous Xenon arc lamp and a microsecond-lamp, respectively. All the measurements were carried out at room temperature. The samples cut from the as-grown and post-annealed crystals were used for XRD and fluorescence spectra measurement. The samples used for absorption spectrum measurement were cut from the post-annealed crystal along three crystallographic axes and polished on both sides with thickness of 1 mm.

3. Results and discussion

3.1. Crystal structure

The XRD patterns of the as-grown and post-annealed Nd:GLNO crystal are shown in Fig. 2. As can be seen, all the diffraction peaks are sharp in the measured range, indicating that the as-grown crystal is of high crystalline quality. Moreover, all the diffraction peaks can be well matched with that of ICSD#20408 (pure $GdNbO_4$) from database, indicating that they belong to the same crystal phase with space group of I2/a and no phase transition appeared after the annealing of 1450 °C. In Nd:GLNO host, La^{3+} and Nd^{3+} are occupied in Gd^{3+} positions and each Gd^{3+} coordinates with eight oxygen atoms and formed a dodecahedron. Each Nb^{5+} coordinates with four oxygen atoms and formed a tetrahedron. The atoms coordinate mode in $GdNbO_4$ is shown in Fig. 3.

3.2. Absorption spectrum

The room temperature absorption spectrum of Nd:GLNO crystal in the wavelength range of 320–950 nm along three crystallographic axes is shown in Fig. 4. The main absorption peaks around 355, 435, 479,

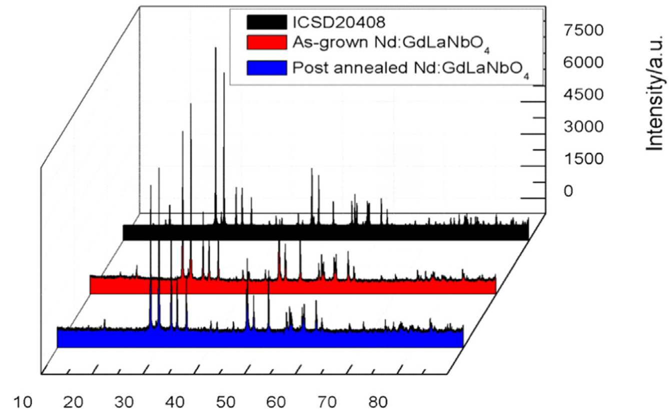

Fig. 2. XRD diffraction pattern of as-grown Nd:GLNO crystal and post-annealed Nd:GLNO crystal, and $GdNbO_4$ standard pattern (ICSD#20408).

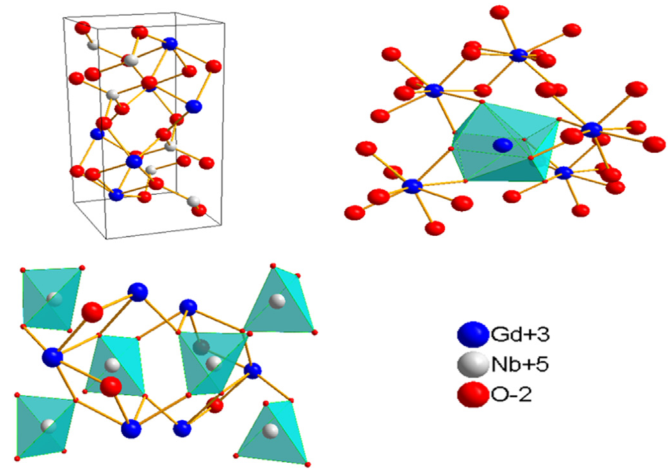

Fig. 3. The atoms coordinate mode in $GdNbO_4$.

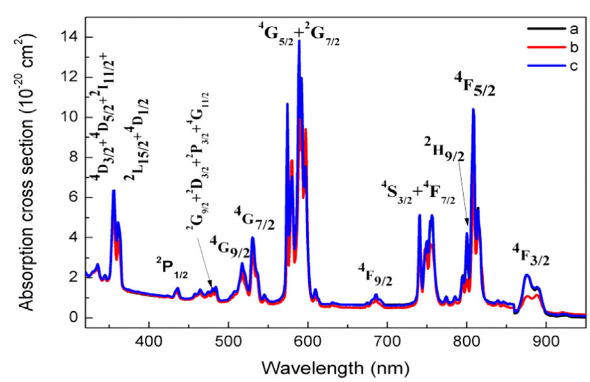

Fig. 4. Absorption spectrum of Nd:GLNO crystal along three crystallographic orientation.

516, 531, 589, 686, 748, 195, 808, and 874 nm are corresponding to the transitions from the ground state $^4I_{9/2}$ to the excited states $^4D_{3/2} + {}^4D_{5/2} + {}^2I_{11/2} + {}^2L_{15/2} + {}^4D_{1/2}$, $^2P_{1/2}$, $^2G_{9/2} + {}^2D_{3/2} + {}^2P_{3/2} + {}^4G_{11/2}$, $^4G_{9/2}$, $^4G_{7/2}$, $^4G_{5/2} + {}^2G_{7/2}$, $^4F_{9/2}$, $^4S_{3/2} + {}^4F_{7/2}$, $^2H_{9/2}$, $^4F_{5/2}$, and $^4F_{3/2}$, respectively. Moreover, the Nd:GLNO crystal along *c*-orientation exhibit a strongest absorption at 808 nm, and the absorption cross section is calculated to be $10.49 \times 10^{-20}\,cm^2$ (The calculation is similar to that we reported in Ref. [15]).

The absorption spectrum of *b*- and *c*-orientation Nd:GLNO and Nd:YAG at around 808 nm is shown in Fig. 5. As can be seen, the full width at half maximum (FWHM) of Nd:GLNO is about 5–13 nm, which