

Spectral Analysis and Growth of Nd:YLF Crystal

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Abstract-

Nd: YLF polycrystalline raw materials were synthesized by a dry method and Nd:YLF laser crystal was grown by IF induction Cz method. Its process parameters were these: a pulling rate of 1 mm/h, the crystal rotation speed of 15 r/min and 10^{-2} Pa degree of vacuum. The absorption and fluorescence spectra of crystal indicates that the Nd:YLF crystal has strong absorption around 808nm at room temperature which belong to commercial laser diode band and under the 808nm diode laser pumped, the fluorescence emission peaks of Nd:YLF crystal are located at 1050 and 1300nm (${}^4F_{3/2} \rightarrow {}^4I_{11/2}$) have stronger emission.

Keywords-Nd: YLF; Crystal growth; spectral analysis

I. INTRODUCTION

In recent years, the development of solid-state laser is characterized by diversity, multi-wavelength technology. The yttrium lithium fluoride crystal which has good optical performance has become one of the hot laser crystal. As a kind of high efficiency laser material that fit a number of important laser applications, YLF crystals have excellent material characteristics and spectral properties, when incorporated into a variety of rare earth ions and activated sensitizer ions, it can be obtained from the UV 0.3 μ m to mid-infrared 3.9 μ m more than 20 band infrared laser transition, etc.^[1-3].

Nd:YLF crystal is in a tetragonal with space group $I_{41/a}$, a negative uniaxial crystal with scheelite structure, lattice parameter of $a=0.526$ nm, $c=1.094$ nm. It can produce 1.047 and 1.053 μ m laser wavelength, which 1.053 μ m wavelength matches Nd doped phosphate glass laser wavelength, it is also an effective working substance for laser oscillator and preamp in laser fusion device^[4,5]. This crystal has a long life, a relatively wide width, a low thermal lensing effect and natural birefringence to promote the Nd:YLF laser development. Compared to Nd:YAG laser, Nd:YLF solid-state laser is easy to achieve laser technology such as mode-locked, tune Q, frequency, pulse compression. Nd: YLF solid state laser has a high energy storage, high pulse repetition frequency and narrow giant-pulse width. The continuous clamping efficiency of Nd:YLF is 5 times higher YAG solid-state lasers, single-mode output of single-lamp-pumped reached to 22W Nd:YLF solid-state lasers have been used in laser fusion, regenerative amplifier, synchronously pumped dye lasers, laser micromachining, optical pulse modulation, etc.^[6-8]. It will be also used in laser spectroscopy, nonlinear optics, free-space

communications and other fields. We used a dry method to optimize the process parameters of raw materials ratio and synthesize YLF polycrystalline material. And we used medium frequency induction heating pulling method to grow the Nd:YLF laser crystal, research the spectral characteristics of the crystal and analyzed the crystal doped ions in energy level transition.

II. EXPERIMENT

Since the growth of Nd:YLF crystal demanding purity raw materials, the chemical reagents LiF, YF₃ and NdF₃ were selected by the purity of 99.999%. The polycrystalline materials were prepared by the dry method. Under HF atmosphere, rare earth fluorides were treated by purification processing in high temperature. Put 5N rare earth oxide powder after 130°C burning in platinum boat of FS-10 fluoride furnace, under flowing HF atmosphere at 600°C, which will obtain rare earth fluoride NdF₃ after reaction.

The polycrystalline materials NdF₃ and LiF, YF₃ which were according to the ratio of LiF:YF₃=53:47 were prepared by the dry method, in which Nd doped mole fraction was 1%, after mixing placed in platinum crucibles, and used induction heating Cz method to grow Nd:YLF crystal, the parameters of the growth of crystal were those a pulling rate of 1mm/h, the crystal rotation speed of 15r/min, 10^{-2} Pa degree of vacuum and the growth cycle of 336 h. In order to prevent the oxidation and volatilization of fluorides, it was grown in the volume ratio of Ar (90%) and CF₄(10%) atmosphere and the cooling rate was 30°C/h. The size of Nd:YLF crystal is about $\phi 26\text{mm} \times 150\text{mm}$.



Fig.1 Nd:YLF crystal

III. RESULTS AND DISCUSSION

A. Purification of rare earth fluoride

Due to the presence of water vapor in the environment, fluoride raw materials readily adsorb moisture and hydrolyze at high temperatures. Also easy to generate oxide impurities, forming oxygen contamination, which is difficult to grow high-quality fluoride crystals. If use the fluoride crystal growth of untreated raw material directly, there will be a lot of white inclusions at the crystal surface. In order to obtain high-quality fluoride laser crystal, we must use the raw materials that not contain moisture and other impurities. It was found that the smaller the particle size of Nd_2O_3 is, the more adequate response is. When the particle size of the raw material or the feeding amount is larger, the reaction is incomplete, which will be residual oxide. When the particle size of REF_3 is larger, the surface area of it is smaller, which is more difficult to hydrolyze. Therefore, REF_3 must be stayed under the atmosphere of HF , heated and melted at 1200°C , in order to ensure crystal quality. Therefore, we must first let the YF_3 rare earth fluoride to be high-temperature purification treatment under the atmosphere of HF , in order to grow high-quality YLF crystal. Rare earth fluoride or the raw material of long-term storage, which is also required to carry out a fluorination treatment before using, so that the residual oxide, fluorine oxide, and anionic impurities will be removed.

B. XRD

The crystal structure was analyzed by X-ray diffraction (XRD) with a Rigaku D/max-rA revolving target XRD apparatus, using a $\text{Cu K}\alpha$ ray ($\lambda=0.154\ 056\ \text{nm}$) as the radiant. The tube voltage was 50 kV and the tube current was 150 mA, and the apparatus had a graphite monochromator. The result of powder XRD analysis for Nd:LYF crystal is shown in Fig. 2, and the diffraction peaks were assigned. Compared with JCPDS card (17-0874), the x-ray diffraction spectrum shows that the diffraction peaks and relative intensity of the crystal sample is very similar to LYF. Therefore, the crystal belongs to a tetragonal phase with a space group $I41/a$.

$$d = \frac{1}{\sqrt{\frac{h^2 + k^2}{a^2} + \frac{l^2}{c^2}}} \quad (1)$$

According to formula (1) for cell parameters of tetragonal systems, the cell parameters of the Nd:LYF crystal are $a=5.221\text{\AA}$, $c=10.978\text{\AA}$ and $Z=4$. The dopant rare earths substitutionally enter the Y^{3+} sites, with local symmetry S_4 .

C. Absorption Spectroscopy

The absorption spectrum of the square slice sample was measured with ultraviolet (UV) spectrophotometer (Model UV360, SHIMADZU Company, Japan) in the 350-900nm range at room temperature. Fig.3 is the absorption spectra of the Nd:YLF crystal within the wavelength range from 350nm to 900nm. From Fig.3 it sees that the crystal has eight main absorption bands which is corresponding to the transitions of Nd ions 4f shell electrons from the ground state $^4I_{9/2}$ to every excited state state $^2P_{1/2}$, ($^2G_{9/2}$, $^2D_{3/2}$, $^2P_{3/2}$, $^4G_{11/2}$), ($^4G_{9/2}$, $^4G_{7/2}$), $^4G_{5/2}$, $^4F_{9/2}$, ($^4S_{3/2}$, $^4F_{7/2}$), $^4F_{5/2}$, $^2H_{9/2}$, $^4F_{3/2}$. The transitions of Nd ions belong to narrow band sharp line 4f-4f transitions. Due to the outer electrons in 5s and 5f have shielding effect on electrons in 4f, the electrons in 4f is little interrupted by the crystal field, thus making the spectra of dopant ions is close to free ions.

The absorption coefficient of Tm^{3+} ions can be calculated as follows:

$$\alpha = \frac{\ln\left(\frac{I_0}{I}\right)}{L} = \frac{2.303OD}{L} \quad (2)$$

where OD is optical density, L is the thickness of the sample(cm). The relation between absorption cross section and absorption coefficient can be expressed as follows:

$$\sigma_a = \frac{\alpha}{N_0} \quad (3)$$

where N_0 is the number of absorption center per volume.

The absorption coefficient and absorption cross section at the strongest absorption peak of 808nm is $5.62 \times 10^{-21}\ \text{cm}^2$.

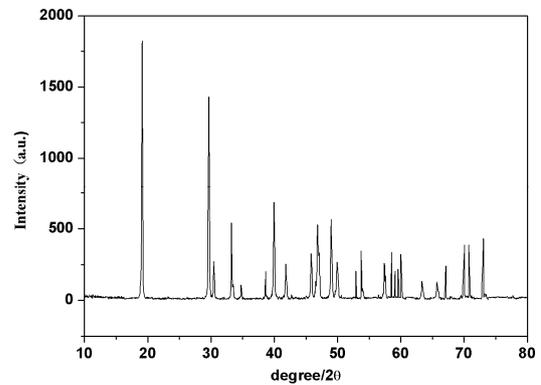


Fig.2 XRD of Nd:YLF

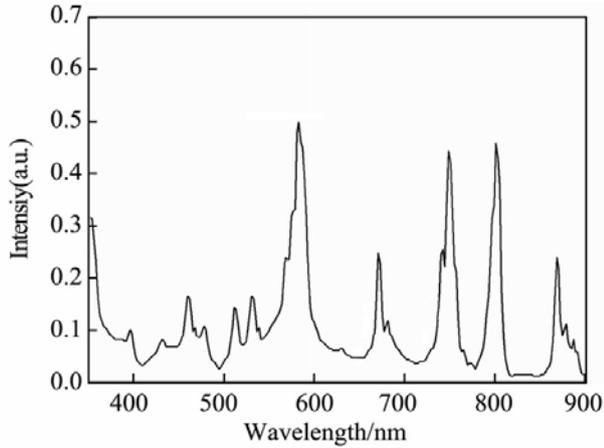


Fig.3 Absorption spectrum of Nd:YLF

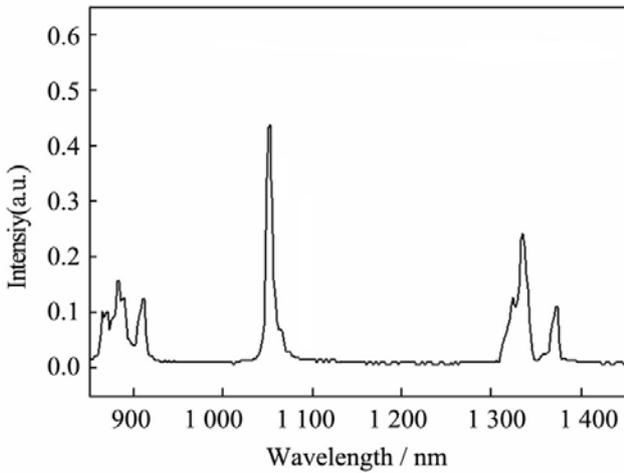


Fig.4 Emission spectrum of Nd:LiYF

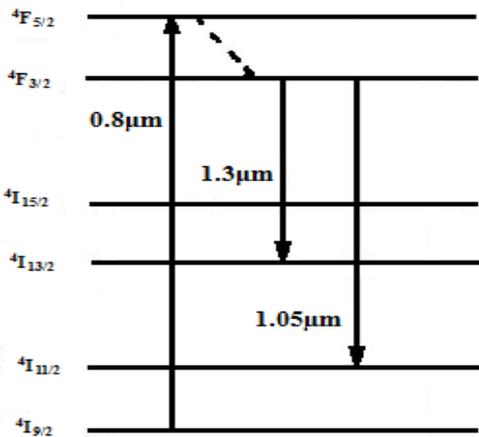


Fig.5 Energy level diagram of the Nd³⁺ ions

D. Emission spectrum

The fluorescence spectrum was measured with a fluorescence spectrometer (Model FluoroLog-3, Horiba Company, Japan) in the 850–1450 nm range at room

temperature, and with the wavelength of 808 nm excited by an excitation source. Fig.4 shows the emission spectra of Nd:YLF crystal was obtained by the 808nm diode laser pumped. Fig.4 shows a level transition pattern of the crystal 1.0μm radiation wavelengths includes 1047nm and 1053nm, corresponding to the $^4F_{3/2} \rightarrow ^4I_{11/2}$ transition, and 1047nm wavelength has maximum light intensity.

It is calculated by the following formula^[9] for fluorescence emission cross section of the crystal:

$$\sigma_{em}(\lambda) = \frac{\lambda^5 \eta I(\lambda)}{8\pi n^2 c \tau \int \lambda I(\lambda) d\lambda} \quad (4)$$

where c is the speed of light, n is the refractive index, η is the radiative efficiency that can be estimated from the comparison between the theoretical radiative and the fluorescence lifetime, $I(\lambda)$ represents the experimental emission intensity as a function of the wavelength.

According to Eq.(4), the IR transition is a broad emission band at about 1047 nm and 1053nm. The maximum emission cross-section of the transition is $1.8 \times 10^{-19} \text{cm}^2$ and $1.2 \times 10^{-19} \text{cm}^2$ near 1047 nm and 1053nm.

The stimulated emission cross section corresponding to 1047nm wavelength ($1.8 \times 10^{-19} \text{cm}^2$) is 1.5 times bigger 1053nm ($1.2 \times 10^{-19} \text{cm}^2$). Therefore the laser resonator that cut A-axis of crystal was used, the maximal output gain was obtained in 1047nm wavelength, the crystal which was cut into the Brewster angle or tilt mirrors method to select 1053nm output by adding Brewster piece to the chamber. Crystal which was in the vicinity of 1.3μm has strong emission peaks corresponding to $^4F_{3/2} \rightarrow ^4I_{13/2}$ transition. Fig.5 Energy level diagram of the Nd³⁺ ions

IV. CONCLUSIONS

Using the dry method, designed the LiF:YF₃=53:47 ratio, synthesis of Nd:YLF polycrystalline materials, the use of intermediate frequency induction Cz method, designed the suitable temperature field, select the pull rate is 1mm/h, the crystal speed of 15r/min, vacuum degree of 10^{-2}Pa , the growth of Nd:YLF laser crystal 26mm 150mm. At room temperature, crystals have strong absorption peaks in the near 808nm, using 808nm laser diode pumped Nd:YLF crystal has a strong emission peak at around 1.05μm and 1.3μm, corresponding to $^4F_{3/2}$, $^4I_{11/2}$ and Nd³⁺ ions $^4F_{3/2}$, $^4I_{13/2}$ transition.

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