

Temperature effect on emission lines and fluorescence lifetime of the ${}^4F_{3/2}$ state of Nd:YVO₄

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By measuring the absorption and fluorescence spectra and the fluorescence lifetime of ${}^4F_{3/2}$ state of Nd³⁺ ions in YVO₄ (2 at.-%) crystal at different temperature, the effects of temperature on the spectra and the lifetime of ${}^4F_{3/2}$ state have been investigated. As the temperature is increased, the line width of the ${}^4F_{3/2} \rightarrow {}^4I_{11/2}$ transitions is found to increase and the spectral line toward the longer wavelength, which are duo to the ion-phonon interaction. The variation fluorescence lifetime of the ${}^4F_{3/2}$ state of Nd:YVO₄ is found to be anomalous in the measured range 8 – 300 K. It is about 81 μ s at room temperature and decreases to 30 μ s at 8 K. The experimental results are explained by ascribing to the thermal mixing between the two Stark levels of ${}^4F_{3/2}$ state with different lifetime.

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In the past several years, the powerful diode lasers have generated intense interests in the development of diode-pumped, high efficient, *Q*-switched laser systems. As a solid-state material, triply ionized neodymium-doped yttrium orthovanadate (Nd³⁺:YVO₄) has many good performances superior to those of standard Nd³⁺:YAG^[1–5] such as high-stimulated emission cross sections and absorption coefficient, high Nd-doped concentration and broad absorption band. So it is an ideal material for laser diode pumped solid-state lasers.

The spectroscopic and laser properties for Nd³⁺:YVO₄ have been studied by many people. The first study of a laser using Nd:YVO₄ was made in 1966 by O'Conner who reported a pulsed-laser threshold near 1 J for 1.06 μ m^[3]. Lomheim presented the intensity parameters, radiative lifetime and quantum efficiency of the ${}^4F_{3/2}$ state^[6]. The crystal-field analysis and investigation have been carried out^[7–9]. Measurements of the temperature and concentration dependence of the lifetime of the ${}^4F_{3/2}$ level in Nd:YVO₄ crystals have been performed^[10]. The studies indicated that the fluorescence lifetime shortened as the Nd:YVO₄ crystal temperature was lowered below room temperature, which are contrary to what is normally observed upon lowering the temperature in other crystals, namely the lifetime either remains constant or increases. Nevertheless, the variation of lifetime was not obvious and there was a simple discussion presented by J. G. Sliney^[10].

For laser action, the thermal broadening and shift of the laser line have a significant meaning since these are closely related to the light amplification gain, output frequency stability, and thermal tunability of the laser. The variation of fluorescent lifetimes with the temperature is also significantly important for many *Q*-switched and other operations of Nd:YVO₄ lasers. In this paper, the low temperature absorption spectra and emission spectra of Nd:YVO₄ single crystals are measured. The temperature dependences of the fluorescence lifetime for the ${}^4F_{3/2} \rightarrow {}^4I_{11/2}$ inter-manifold transitions of Nd³⁺ ions in this host have been studied. The reasons of abnormal variation of the fluorescence lifetime of Nd:YVO₄ with the temperature increase are discussed.

Single crystals of Nd:YVO₄ were grown from iridium crucibles by Czochralski technique. The sample was doped with 2 at.-% of Nd³⁺ in the melt. The optical quality of the material was found to be good. During the growth of Nd³⁺:YVO₄ crystals, the substitution of Y³⁺ by Nd³⁺ is accomplished easily because the dimensional, chemical, and physical properties of the two ions are quite similar. The sample used for spectroscopic measurements was optically polished and the thickness of the sample was 1.0 mm.

A Fourier-transform spectrometer (Model Nexus 870 FT-IR, Nicolet) collected both absorption and photoluminescence data, the latter being excited by the 514.5-nm line of an argon ion laser. The beam splitter was quartz and the detector was silicon photo-diode. The spectral resolution was 4 cm⁻¹ in all measurements. Emission decay curves were obtained by pulse excitation with the 589-nm line of a Nd:YAG laser pumped dye laser (pulse duration 10 ns). The emitting light was detected through a 0.5-m monochromator with a photomultiplier. Luminescence was recorded in a 500-Hz digital oscilloscope. For the low temperature measurements, the Nd:YVO₄ sample was mounted at the cold finger of a CTI model 22, a closed-cycle helium cryogenic refrigerator, capable of controlling temperature from about 8 to 300 K. The temperatures were controlled by a Lake Shore model 330 temperature controller and measured by a silicon diode sensor attached to the base of the sample holder.

The absorption spectra in several spectral regions were investigated, special attention was paid to absorption in ${}^4F_{5/2}$ that is used as usual pump level. Figure 1 shows the low temperature (77 K) and room temperature absorption spectra for the ${}^4I_{9/2} \rightarrow {}^4F_{5/2}$ transitions of Nd:YVO₄ sample with 2.0 at.-% Nd concentration. The solid line represents absorption spectrum at 77 K and the dotted line indicates absorption spectrum at 300 K. The main absorption peak is 809 nm, corresponding to ${}^4I_{9/2}(1) \rightarrow {}^4F_{5/2}(1)$ transition. The remaining absorption lines in the spectrum are thermal replicas of the main lines, i.e., they originate from thermally populated excited levels within the ${}^4I_{9/2}$ manifold, some of which originating from the highest level of the ${}^4I_{9/2}$ manifold

are frozen out at 77 K. The absorption linewidth at 809 nm is 1.0 nm at low temperature 77 K, while 1.8 nm at 300 K, which is broader than that of Nd:YAG and is suitable for diode-pumping. The absorption linewidths increase and the position of absorption lines slightly shift toward the longer wavelength with increasing temperature. Similar characteristics were observed in the other absorption regions.

The fluorescence spectra at 77 and 300 K for the ${}^4F_{3/2} \rightarrow {}^4I_{11/2}$ transition of Nd^{3+} in YVO_4 are shown in Fig. 2. The solid line represents the fluorescence lines at 77 K and the dotted line indicated the fluorescence lines at 300 K. YVO_4 belong to the Zircon-type structure with tetragonal symmetry (space group D_{4h}^{19}). The optically active neodymium ion is located on the Y^{3+} position with a D_{2d} site symmetry, which is responsible for the polarized transitions of Nd^{3+} and the plane-polarized laser output useful in many applications. Due to the low symmetry of the local crystal field each $|J\rangle$ level of the $4f^3 \text{Nd}^{3+}$ configurations splits into $(2J+1)/2$ Kramers doubles in YVO_4 crystal. A total of 10 emission bands are observed at 77 K in Fig. 2. The 1064.0-nm line designated as number 2 is the most intense line corresponding to the ${}^4F_{3/2}(1) \rightarrow {}^4I_{11/2}(1)$ transition at low temperature. All the lines shift to the red and the linewidths of all the lines increase with increasing temperature. The main emission line shifts from 1064.0 nm at 77 K to 1064.5 nm at 300 K. The width (FWHM) of the

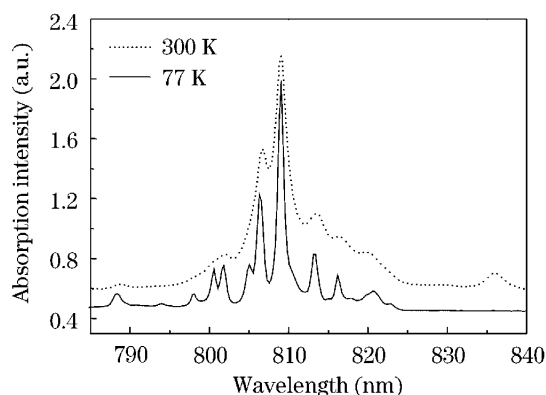


Fig. 1. Absorption spectra of ${}^4I_{9/2} \rightarrow {}^4F_{5/2}$ transitions for Nd^{3+} in YVO_4 crystal at 300 K (dotted line) and 77 K (solid line).

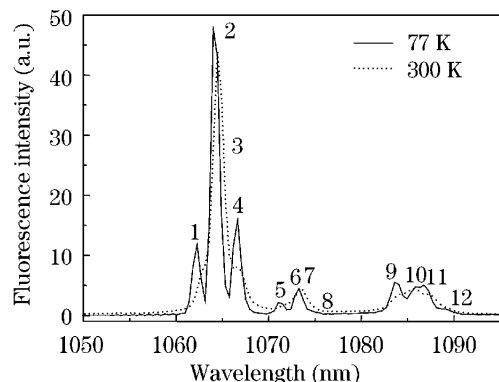


Fig. 2. ${}^4F_{3/2} \rightarrow {}^4I_{11/2}$ emission spectra of $\text{Nd}^{3+}:\text{YVO}_4$ crystal at 300 K (dotted line) and 77 K (solid line).

1064.0-nm line increased from 1.1 nm at 77 K to 1.4 nm at 300 K.

The line shifts are due to the stationary effect of the ion-phonon interaction^[11]. Electron-phonon interactions perturb various electronic states, changing their wave functions and energies. The greater the distance from neighboring atoms, the lower the potential of the crystal field of an impurity ion and the smaller the Stark splitting of its multiplets as the temperature of the crystal increase. The temperature dependent line broadening mechanism arises from the interaction between the impurity ions and the crystalline host lattice vibrations. The broadening of an energy level is mainly due to the crystal strain inhomogeneity, direct one-phonon processes, multiphonon processes, and Raman phonon scattering processes. At the lowest temperature, the measurable line width of a radiative transition is in general accounted for the microscopic strains of the crystal, which are inhomogeneous due to their random nature and independent on temperature, thus giving rise to a Gaussian line shape. The shape of the spectral lines of the $\text{Nd}:\text{YVO}_4$ are found to be Lorentzian at 77 K and room temperature. So the line broadening arising from crystal strain inhomogeneity can be neglected. Multiphonon emission processes can take place between two levels whose energy difference is greater than the greatest energy of the available phonons, and has been shown to be essentially temperature independent and negligible in the temperature range of interests^[11]. Hence the thermal broadening of emission lines of $\text{Nd}:\text{YVO}_4$ are mainly related to the direct one-phonon processes and Raman phonon scattering processes due to the ion-phonon interaction.

${}^4F_{3/2} \rightarrow {}^4I_{11/2}$ emission decay has been measured as a function of temperature from 8 to 300 K. Luminescence was excited non-resonantly in the intense ${}^4G_{5/2}$ at 589 nm. Decays of emission measured at different temperature for $\text{Nd}:\text{YVO}_4$ are depicted in Fig. 3. All the decay curves are slightly nonexponential, which is ascribed to the higher Nd^{3+} concentrations in the samples (2 at.-% Nd-doped content). The value of the measured decay time is 81 μs at room temperature and less than the decay time of 1 at.-% Nd-doped YVO_4 crystal, which indicates that concentration quenching is taking place. For Nd^{3+} doped samples the concentration quenching are mainly due to cross relaxation between identical ions and

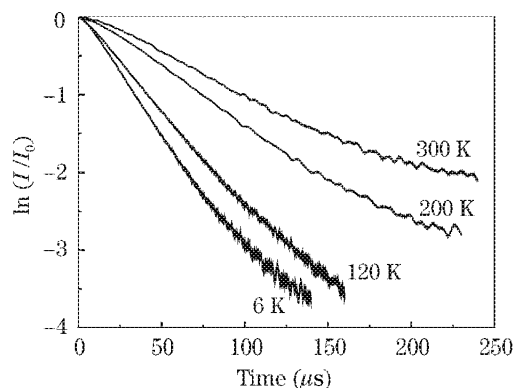


Fig. 3. Emission decay of the ${}^4F_{3/2}$ level for $\text{Nd}^{3+}:\text{YVO}_4$ (2 at.-%) at different temperature.

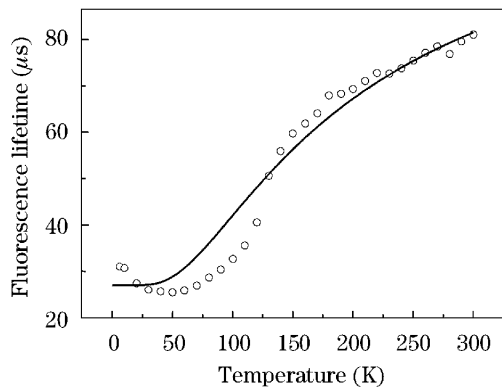


Fig. 4. Temperature dependence of the ${}^4F_{3/2}$ level fluorescence lifetime for Nd $^{3+}$:YVO $_4$ (2 at.-%) crystals. The solid line represents the fit line to the experimental results.

energy migration from the excited ion to a nearby similar ion, which cause the departures from exponential for the decay curve of Nd:YVO $_4$. The energy gap of Nd:YVO $_4$ between ${}^4F_{3/2} \rightarrow {}^4I_{15/2}$ and ${}^4I_{9/2} \rightarrow {}^4I_{15/2}$ is about 411 cm $^{-1}$ and larger than that of Nd:YAG (about 205 cm $^{-1}$). Thus there is a lower cross relaxation rate and slighter exponential departure. It is also found that the decays of emission intensity are faster at low than at high temperature for the Nd:YVO $_4$. The temperature dependence of the lifetime for the Nd:YVO $_4$ sample is given in Fig. 4. The decay time of ${}^4F_{3/2}$ state of Nd $^{3+}$ shows obvious temperature dependence. The low temperature lifetime remains essentially constant around 27 μ s up to 60 K where it starts to increase. The variation is abnormal comparing to other crystals, of which the lifetimes either remain constant or decrease with the temperature increasing. This is ascribed to the effect on the emission lifetime of the thermal population of the most energetic ${}^4F_{3/2}$ Stark level.

In general, the temperature dependence of lifetime for the ${}^4F_{3/2}$ state of Nd $^{3+}$ ion may change under the influence of another factor^[12]. In lower symmetry crystal field of Nd $^{3+}$ local environment, the ${}^4F_{3/2}$ state splits into two manifold and several multiples (${}^4F_{5/2}$, ${}^4H_{9/2}$ and so on) lie not so far above this metastable ${}^4F_{3/2}$ state. If their luminescence lifetimes are significantly different from that of the ${}^4F_{3/2}$ state, then an increase in temperature may cause the static population differences between these multiplets and the ${}^4F_{3/2}$ state to decrease, and may change the observed luminescence lifetime of that state. Because the energy gap of the Nd:YVO $_4$ between the ${}^4F_{3/2}$ and ${}^4F_{5/2}$ manifolds is approximately 982 cm $^{-1}$, the influence of the latter on the lifetime of the metastable state will not be especially noticeable below about 1000 K. Then the temperature dependence of lifetime will be connected only with the different of spontaneous radiation probabilities for transition from the components of the ${}^4F_{3/2}$ state itself. The very little stark splitting of ${}^4F_{3/2}$ state is observed for Nd $^{3+}$ in YVO $_4$ comparing to Nd:YAG. As the Fig. 2 shown, the energy gap between the line designated number 1 (${}^4F_{3/2}(2) \rightarrow {}^4I_{11/2}(1)$) and the line designated number 2 (${}^4F_{3/2}(1) \rightarrow {}^4I_{11/2}(1)$) is only 15 cm $^{-1}$. So the

expression for the total probability of spontaneous transitions of ${}^4F_{3/2}$ state can be written^[12]

$$A_i = \frac{\sum_i A_i n_i}{\sum_i n_i} = \frac{A_1 n_1 + A_2 n_2}{n_1 + n_2}, \quad (1)$$

where n_1 and n_2 are the population of the upper level and lower level for the ${}^4F_{3/2}$ state, respectively. If the spontaneous transitions A_1 for the upper level is larger than A_2 for the lower level, the lifetime will be reduce, if not the lifetime will be increased with the temperature increasing. As n_1 and n_2 are in thermal equilibrium by phonon exchange. According to the thermal equilibrium of Boltzmann population

$$\frac{n_2}{n_1} = \exp(-\Delta E/kT), \quad (2)$$

where ΔE is the energy gap between the two sublevels of the ${}^4F_{3/2}$ state, k is Boltzmann's constant, T is the temperature, and A is ratio constant. The lifetime of the thermally mixed level is then given by

$$\tau = \frac{1}{A_i} = \frac{1 + \exp(-\Delta E/kT)}{(1/\tau_1) + (1/\tau_2) \exp(-\Delta E/kT)}, \quad (3)$$

where τ_1 and τ_2 are the lifetimes of the two thermalized levels. Equation (3) is applied to the date of the temperature dependence of lifetime of Nd:YVO $_4$. The solid line in Fig. 4 represent the fit to date with $\tau_1 = 28 \mu$ s and $\tau_2 = 335 \mu$ s. The agreement between experimental points and theoretical curves is not very good. In Eq. (3) it has been assumed that the transition probabilities from excited level to all the remaining levels lying below it are temperature independent. The presume is not absolutely correct, which possibly lead to the departure between theoretical curve and measured data. Moreover, for Nd $^{3+}$ in YVO $_4$ ^[3], in addition to the strong static distortions there are also dynamic distortions caused by low-frequency lattice vibrations which are observed at 1400, 1700 and 2500 cm $^{-1}$. Both of these distortions cooperate to alter the crystal-field selection rules and can allow dipole transitions to occur, which can affect the lifetime of ${}^4F_{3/2}$ state and not be considered in the Eq. (3).

The experimental results show that the linewidths and positions of emission line of Nd:YVO $_4$ crystal are temperature-dependent. The main emission line is observed to shift from 1064 nm at 77 K to 1064.5 nm at 300 K. The width increased 0.3 nm from 77 to 300 K. They are related to Raman scattering of phonos and direct one phono processes due to the interaction between the impurity ions and the crystalline host lattice vibrations. The fluorescence lifetime of ${}^4F_{3/2}$ state for the Nd:YVO $_4$ increase obviously with the temperature increasing. This is mainly ascribed to thermal mixing between the two Stark levels of the ${}^4F_{3/2}$ state, and the lifetime of the upper level is larger than the lower level.

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