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OPTICAL TRANSITION OF TRIVALENT NEODYMIUM (Nd^{3+}) IN THE ANISOTROPIC CRYSTAL LITHIUM NIOBATE

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ABSTRACT

The absorption spectroscopic analysis of the radiative transitions of Nd-doped $LiNbO_3$ has been analysed. The line strengths of several transitions from the ground state to the excited state manifolds are evaluated from the measurement of the polarized absorption spectra and are analyzed using the Judd-Ofelt (J-O) theory. The transition-matrix elements for Nd^{3+} were calculated by using intermediate coupling coefficient and the results were used to obtain the J-O parameters. It is found that the intensity parameters (J-O parameters) of this crystal Ω_2, Ω_4 and Ω_6 are 2.1×10^{-20} cm^{-2}, 5.6×10^{-20} cm^{-2}, and 7.1×10^{-20} cm^{-2} respectively, with the goodness, $\delta = 0.23 \times 10^{-20}$. Meanwhile, the spectroscopic quality factor, Q is found to be 0.79. The radiative lifetimes, the branching ratios and the line transition strengths have been calculated and were found to be dependent on the transition level. The radiative quantum efficiency, η is calculated by using multiphonon relaxation rates and it is found that the lasing transition at $^4F_{3/2}$, η is around 0.83.

INTRODUCTION

The attention on the $LiNbO_3$ nonlinear crystal as a laser host for rare-earth ions has increased in the past few years [1]. In particular is the Nd:$LiNbO_3$ crystal which could be an excellent candidate for solid state laser due to the combination of the nonlinear, acousto-optic, and electro-optic properties of $LiNbO_3$ and the gain properties of the Nd^{3+} ion. The combination of these properties will permit small compact lasers with several functions which is useful in the integrated optics.

$LiNbO_3$ is a uniaxial crystal with the C_{3v} space group symmetry. The Nd^{3+} ions can substitute into either Li^+ or Nb^{5+} sites with nearly equal probability. In both lattice sites, are located within distorted oxygen octahedral, the crystal electrostatic field is not centrosymmetric [2]. The anisotropic condition is suggested to change the probability of parity-forbidden $f \rightarrow f$ transitions. Objectives of this paper : to study the spectral characteristics and to quantify the radiative transitions between different excited levels of Nd^{3+} ions in $LiNbO_3$ host crystal, specify at the lasing transition.

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THEORITICAL CONSIDERATION

The optical absorption spectra of Nd^{3+} in crystals consist of several groups of lines corresponding to transitions between the Stark components of ${}^{2S+1}L_J$ states inside the $4f^3$ electronic configuration of the ion. According to the Judd – Ofelt (JO) theory [3,4], the line strength for a transition between an initial J manifold $\left|4f^n[SL],J\right\rangle$ and final J' manifold $\left|4f^n[S'L'],J'\right\rangle$ is given by,

$$S(J,J') = \sum_{\lambda=2,4,6} \Omega_\lambda \left|\left\langle 4f^n[SL],J \left\| U^{(\lambda)} \right\| 4f^n[S'L'],J' \right\rangle\right|^2 \quad (1)$$

where Ω_λ are the JO parameters (which are host dependence) and $\left|\left\langle \left\| U^{(\lambda)} \right\| \right\rangle\right|^2$ are the matrix elements which are independent of the host material. The host dependence of JO parameters are represented by three phenomenological $\Omega_{2,4,6}$ which contain crystal-field parameters, interconfigurational radial integrals and the energy denominators from the perturbation expansion of the wave function.

The experimental transition strengths can be calculated by determining the integrated absorption coefficient for transitions between the ground state and the upper levels. This coefficient (known as absorbance Γ) can be written in term of a line strength as,

$$\Gamma = \frac{4\pi^2 N \alpha_f \bar{\lambda}\left(n^2+2\right)^2}{3(2J+1)9n} S(J,J') \ , \quad (2)$$

where N is the rare earth ions concentration, n is the refractive index of the materials, $\bar{\lambda}$ is the average wavelength of the transition and α_f is the fine-structure constant. Equation (2) can then be fitted using a least-squares fitting, allowing the extraction of the JO parameters Ω_λ. These parameters may then be used to calculate the strength of any radiative transition for the particular dopant-host combination.

Moreover, the radiative lifetimes τ_R and the fluorescence branching ratios β, can be determined by a radiative transition probabilities $A(J,J')$ using the relation,

$$1/\tau_R = \sum_{J'} A(J,J') \quad (3)$$

and

$$\beta(J,J') = \tau_R \, A(J,J') \quad (4)$$

with

$$A(J,J') = \frac{32\pi^3 \alpha_f c n\left(n^2+2\right)^2}{3(2J+1)9\bar{\lambda}^3} S(J,J') \quad (5)$$

From equation (3), the quantum efficiency η may be calculated as,

$$\eta = \frac{\tau}{\tau_R} \quad (6)$$

where τ is the fluorescence lifetime.

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EXPERIMENTAL TECHNIQUES

The optical measurements were carried out on a congruent 10 mm thick, z-cut sample of Nd:$LiNbO_3$ provided by CASSIX at room temperature with the Nd^{3+} ions concentration of 8.43 x 10^{-19} cm^{-3}. The polarized absorption and reflection spectra from 300 to 1000 nm were recorded on a UV-Vis-NIR Edward FTM 5 Spectrophotometer, using an undoped sample of similar dimensions in the reference arm. The resolution of the spectrophotometer for these measurements was better than 0.5 nm.

RESULTS AND DISCUSSION

Figure 1 shows the π-polarized and the σ-polarized absorption spectra of Nd:$LiNbO_3$ crystals for several transitions from the ground state to excited levels at room temperature. There are some broadening in the absorption lines and the appearance of supplementary weak lines (hot bands) at the low energy side of each transition. This fact is due to a thermal population of excited levels in the ground state $^4I_{9/2}$. From these absorption spectra, the line strength S_{exp} can experimentally be determined for all the transitions. Meanwhile, knowing that the refractive indices of Nd:$LiNbO_3$, n ≅ 2.347, then line strengths, S_{cal} can be calculated from equation (2). These values are inserted in Table 1.

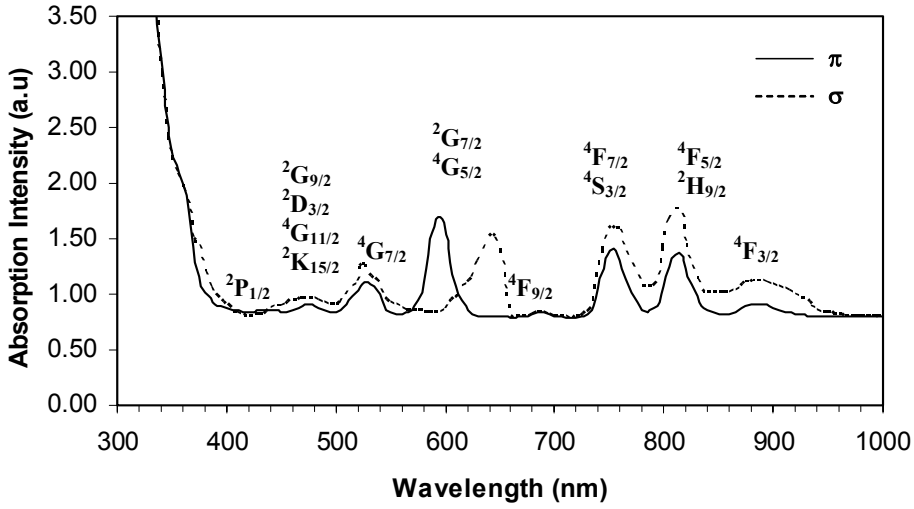

Figure 1: Polarized absorption spectra of Nd:$LiNbO_3$ crystal at room temperature

Table 1: Experimental and calculated line strengths. All transitions are from the $^4I_{9/2}$ level to the levels indicated

Level	Average wavelength (nm)	S_{exp} (x10^{-20} cm^2)	S_{calc} (x10^{-20} cm^2)	Deviation S_{calc}-S_{exp} (x10^{-20} cm^2)
$^4F_{3/2}$	892	1.410	1.702	0.292
$^4F_{5/2}$, $^2H_{9/2}$	815	4.728	5.068	0.340
$^4F_{7/2}$, $^4S_{3/2}$	754	5.204	4.941	-0.263
$^4F_{9/2}$	690	0.309	0.363	0.054
$^4G_{5/2}$, $^2G_{7/2}$	597	5.775	5.782	0.007
$^4G_{7/2}$	528	2.350	2.245	-0.105
$^2G_{9/2}$, $^2D_{3/2}$	476	0.579	0.618	0.039
$^2G_{11/2}$, $^2K_{15/2}$	440	0.189	0.221	0.032
$^2P_{1/2}$				

It should be noted that the deviation, S_{cal}-S_{exp} is small, which indicates the accuracy of the method used.

All, except for the $^4I_{15/2} \rightarrow {}^4I_{13/2}$ transition, were assumed to be electric-dipole in nature. The $^4I_{15/2} \rightarrow {}^4I_{13/2}$ transition which is due to the magnetic-dipole contribution was calculated to be 0.068 x 10^{-20} cm^2. These values were then substracted from the measured (experimental) transition strength to give the purely electric dipole transition strength.

To evaluate the accuracy of the J-O parameters obtained by least-squares fitting, the goodness of fit was calculated according to the following equation,

$$\delta_{rms} = \left(\frac{\sum (deviations)^2}{no.of\ levels - no.\ of\ parameters} \right) \tag{7}$$

The agreement between these values were quite good with δ_{rms} = 0.23 x 10^{-20}.

From the value of line strength S and matrix elements of Nd^{3+} ion [5], the JO parameters can be determined from equation (1) and the parameters are as follows ;

$$\Omega_2 = 2.1 \text{ x } 10^{-20} \text{ cm}^{-2}$$
$$\Omega_4 = 5.6 \text{ x } 10^{-20} \text{ cm}^{-2} \tag{8}$$
$$\Omega_6 = 7.1 \text{ x } 10^{-20} \text{ cm}^{-2}$$

The spectroscopic quality factor Q ($Q = \Omega_4/\Omega_6$) of these parameters may be calculated. In this case, the quality factor, Q is 0.79 which means that the efficiency of the transition $^4F_{3/2} \rightarrow {}^4I_{11/2}$ is enhanced while the efficiency of transition $^4F_{3/2} \rightarrow {}^4I_{9/2}$ is reduced.

Table 2 summarises the calculated radiative transition probabilities A, the radiative lifetimes τ_R of the three energy levels ($^4F_{3/2}$, $^4G_{7/2}$ and $^2P_{1/2}$), and the branching ratios β for each level that have been calculated by using equation (5), equation (3) and equation (4) respectively. From Table 2, it can be seen that the dominant branching ratio for the $^4F_{3/2} \rightarrow {}^4I_{11/2}$ transition is $\beta = 0.52$. This is in agreement with the observance of

laser emission along this channel [6].

Table 2. Calculated radiative transition probabilities A, branching ratios β, and radiative lifetimes τ_R for the $^4F_{3/2}$, $^4G_{7/2}$ and $^2P_{1/2}$

Final J Manifold	**Initial J Manifold**					
	$^4F_{3/2}$		**$^4G_{7/2}$**		**$^2P_{1/2}$**	
	A(s^{-1})	**β**	**A(s^{-1})**	**β**	**A(s^{-1})**	**β**
$^4I_{9/2}$	2755	0.37	4940	0.39	158	0.03
$^4I_{11/2}$	3588	0.52	4820	0.32	1244	0.23
$^4I_{13/2}$	709	0.10	2855	0.21	712	0.11
$^4I_{15/2}$	90	0.01	180	0.01	152	0.03
$^2H_{9/2}$			385	0.04	55	0.01
$^4F_{9/2}$					1497	0.31
$^2G_{9/2}$					233	0.04
τ_R (μs)	136		54		129	

At this point, the overall quantum efficiency from the $^4F_{3/2}$ emitting state can be determined if the fluorescence lifetime is measured. The measured fluorescence lifetime of Nd^{3+} in the Nd:$LiNbO_3$ crystal can be approximated by calculating the nonradiative decay rate (W_{NR}) [7] and is found to be 112.88 μs. Then the quantum efficiency η for this level can be calculated and is equal to 0.83.

CONCLUSIONS

A spectroscopic study of the anisotropic Nd:$LiNbO_3$ crystal has successfully been made. The intensities of the polarized absorption lines have been analyzed using the Judd-Ofelt formalism to evaluate the radiative of the main emission transitions. The lasing transition occurs in the $^4F_{3/2} \rightarrow {}^4I_{11/2}$ transition where the branching ratio β = 0.52 and the radiative quantum efficiency η = 0.83.

The quality factor Q is 0.79 and the value of Ω_6 is large compared to the other two parameters. In the case of neodymium ions (Nd^{3+}) in $LiNbO_3$ crystal, the efficiency of the transition $^4F_{3/2} \rightarrow {}^4I_{11/2}$ is enhanced and the efficiency of transition $^4F_{3/2} \rightarrow {}^4I_{9/2}$ is reduced.

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