

Spectral Properties and Parameters Calculation of Er:LiGdF₄ Crystal

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ABSTRACT

The absorption and fluorescence spectra of Er³⁺:LiGdF₄ crystal was measured at room temperature. Base on the Judd-Ofelt theory, the intensity parameters of Er³⁺ in LiGdF₄ crystal were determined, $\Omega_2 = 0.905 \times 10^{-20} \text{ cm}^2$, $\Omega_4 = 2.47 \times 10^{-20} \text{ cm}^2$ and $\Omega_6 = 4.92 \times 10^{-20} \text{ cm}^2$. The values of the radiative transition probabilities, branching ratios, integrated emission cross-section and radiative lifetimes of excited states of Er³⁺ in LiGdF₄ crystal were calculated. The stimulated emission cross-section was also evaluated for the $^4I_{13/2} \rightarrow ^4I_{15/2}$ transitions. In comparisons with other Er³⁺ doped laser crystals, Er³⁺:LiGdF₄ crystal has potential as a promising laser crystal.

Keywords: Erbium-Doped Yttrium Lithium Gadolinium Fluoride Crystal, Absorption Spectrum, Judd-Ofelt Theory

1. Introduction

Diode-pumped solid-state lasers operating in the eye-safe spectral region around 1.5 μm have been of increasing interest in recent years, for a mass of application fields such as eye-safe compact devices for laser medical, environmental detection, laser radar, electro-optical jamming, remote sensing, optical communication and laser ranging [1-3]. During the last few years Er³⁺-doped materials have been widely investigated for possible laser applications, especially in spectral ranges around 1540 nm ($^4I_{13/2} \rightarrow ^4I_{15/2}$), which have low in optical waveguide and are safe to human eyes [4].

1.5 μm laser emission of Er³⁺ has been investigated in several hosts, both oxides [5,6] and fluorides [7,8]. Furthermore, fluoride hosts possess a low phonon energy, lower emitted threshold, wide-in-wavelength transmission region, lower thermal effects [9,21], resulting in longer lifetimes with respect to oxide crystals, without significant decreasing of the emission cross section values.

In this work, The Judd-Ofelt (J-O) intensity parameters Ω_λ ($\lambda = 2, 4, 6$) were determined by analyzing the room temperature absorption spectra of Er³⁺-doped LiGdF₄ crystal. And the radiative transition probabilities, branching ratios, integrated emission cross-sections and radiative lifetimes of excited states of Er³⁺ in LiGdF₄ were

calculated. In addition, The stimulated emission cross-sections for selected transitions were also calculated. The results show that this crystal may be a preferable candidate for a tunable infrared laser media.

2. Experimental

The starting material was prepared from commercially available LiF and GdF₃ powders of high purity (> 99.999%). As dopants, high purity ErF₃ powder (> 99.999%) was used. The concentration of Er³⁺ in the starting material was 2.1 mol%. As the LiGdF₄ compound melts slightly incongruent and a few LiF evaporate during process of Er:LiGdF₄ growth, the starting material was LiF:GdF₃ = 68:32. All the powders were purified by HF processing in order to prevent OH⁻ contamination.

The growth of Er:LiGdF₄ crystal has been performed with a growth apparatus consisted of DJL-400 Czochralski furnace with conventional resistive heating, special care has been devoted to the quality of the vacuum system, which should have an ultimate pressure limit better under 10^{-3} Pa, the growth process was carried out in a high purity(5N) argon atmosphere. Thereafter, the starting materials were melted at approximately 860°C. The pull and the rotation rate were 0.16 mm/h and 3 rpm. After growth, the crystal was cooled to room temperature at a rate of 10°C /h.

The absorption spectrum of the square slice sample was measured with ultraviolet (UV) spectrophotometer (Model UV360, SHIMADZU Company, Japan) in the 300 - 1800 nm range at room temperature. The fluorescence spectrum was measured with a fluorescence spectrometer (Model Fluoro-Log-3, Horiba Company, Japan) in the 900 - 1700 nm range at room temperature, and with the wavelength of 532 nm excited by an excitation source.

3. Results and Discussion

3.1. Absorption Spectrum

Figure 1 shows the absorption spectrum of Er:LiGdF₄ crystal in room temperature. The spectrum consists of six resolved bands associating with the transitions from the ground state ⁴I_{15/2} to excited states ⁴I_{13/2}, ⁴I_{11/2}, ⁴I_{9/2}, ⁴F_{9/2}, ⁴S_{3/2}, ²H_{11/2}, ⁴F_{7/2}, ⁴F_{5/2}, ⁴F_{3/2}, ²H_{9/2}, ⁴G_{11/2}, ⁴G_{9/2} and ²G_{7/2}. The strong absorption bands at 986 nm and 1540.9 nm are suitable for diode laser pumping. The absorption cross-section σ_a can be determined by the following equation:

$$\sigma_a = \frac{\alpha}{N_0} \quad (1)$$

where α is the absorption coefficient, $\alpha = A/(L \times \log_{10} e)$, A is the absorbance, L is the thickness of the polished crystal, and N_0 is the concentration of Er³⁺ ions in Er³⁺:LiGdF₄ crystal. The absorption cross-section of ⁴I_{15/2} → ⁴I_{13/2} transition can be observed in **Figure 1**. The full width at half maximum (FWHM) at 986 nm and 1540.9 nm is 2.469 nm and 5.0319 nm; the corresponding absorption cross-section is $0.43 \times 10^{-20} \text{ cm}^2$ and $1.09 \times 10^{-20} \text{ cm}^2$, respectively.

3.2. Spectroscopic Analysis (J-O)

Rare-earth doped crystals and glasses analyzed with

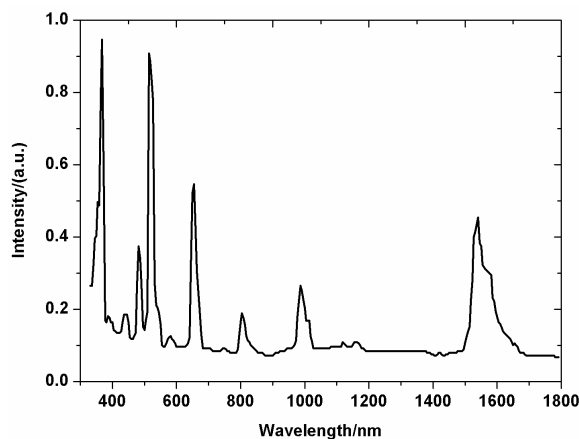


Figure 1. Absorption spectrum of Er:LiGdF₄ crystal.

Judd-Ofelt theory was successfully, especially for determining the branching ratios (β) from one level to other levels [10]. According to the Judd-Ofelt theory [11,12], electronic dipole transitions within the $4f_n$ configuration of a rare-earth ion can be analyzed. The electronic dipole transition line strength $S_{JJ'}$ between two different J states can be expressed as:

$$S_{JJ'} = \sum_{\lambda=2,4,6} \Omega_{\lambda} \left| \langle f_n \varphi J \| U^{(\lambda)} \| f_n \varphi' J' \rangle \right|^2 \quad (2)$$

where J represents the quantum number of the initial state transition, J' represents the quantum number of the terminal state transition, f_n represents the electronic configuration, φ represents the electronic wave functions, $U^{(\lambda)}$ represents the unit tensor element of the J - J' transition, $\langle f_n \varphi J \| U^{(\lambda)} \| f_n \varphi' J' \rangle$ represents the unit tensor reduced element of the J - J' transition and Ω_{λ} represents the phenomenological strength parameters determined by the coordinated property of the host materials.

The relationship between the integral absorption intensity Γ and the spectral line intensity can be described as follows:

$$\Gamma = \frac{\int \sigma d\lambda}{\lambda} = \frac{2\pi^2 e^2 (n^2 + 2)^2}{27 h \epsilon_0 n c (2J + 1)} S_{JJ'} \quad (3)$$

where λ represents the average wavelength of the J - J' transition, n represents the refractive index of the transition wavelength, ϵ_0 represents the vacuum dielectric constant, c represents the vacuum speed of the light, h represents the Planck's constant, e represents the electronic charge and σ represents the absorption cross-section.

The central wavelength absorption peaks correspond to each energy level, the unit tensor element of the J - J' transition. The integral absorption intensity and the spectral line intensity of the Er:LiGdF₄ crystal sample absorption spectrum are shown in **Table 2**. According to the data in **Table 2** and **Formulas (2) and (3)**, the phenomenological strength parameters Ω_{λ} were fitted out as follows: $\Omega_2 = 0.905 \times 10^{-20} \text{ cm}^2$, $\Omega_4 = 2.47 \times 10^{-20} \text{ cm}^2$ and $\Omega_6 = 4.92 \times 10^{-20} \text{ cm}^2$. In formulas (2) and (3), J is equal to 15/2 as the ⁴I_{15/2} energy level of the Er³⁺ ion.

Generally, the intensity parameters can reflect the crystal structure, coordinated symmetry and order properties. The higher the values of the intensity parameters and the stronger the covalent characteristic of the intensity parameters are, the stronger the ionic characteristic of the crystal is.

The spontaneous radiation probability can be determined by the absorption spectrum. In fact, the probability contains the contributions of all kinds of multi-pole moments. Here we only consider the electric dipole moment. In respect to the radiation transition of the multiple excited state $aSLJ$ - $a'SL'J'$, the spontaneous radiation

Table 1. Comparison of the Judd-Ofelt intensity parameters of some Er³⁺ doped laser crystal to those of LiGdF₄.

crystal	$\Omega_2/(\times 10^{-20}\text{cm}^2)$	$\Omega_4/(\times 10^{-20}\text{cm}^2)$	$\Omega_6/(\times 10^{-20}\text{cm}^2)$	Ref.
CaSGG	12.2	7.38	5.1	13
LiNbO ₃	7.29	2.24	1.27	14
YAlO ₃	0.95	0.58	0.55	15
YAG	0.45	0.98	0.62	16
Bi ₂ TeO ₅	0.698	0.174	0.123	17
LaGaO ₃	3.59	2.49	0.44	18
Li ₂ Gd(MoO ₄) ₇	7.93	2.50	2.03	19
LiGdF ₄	0.905	2.47	4.92	This work

Table 2. Integral absorption intensities and spectral line intensities of Er:LiGdF₄ crystal sample.

Transtion	λ/nm	U(2)	U(4)	U(6)	$\Gamma/10^{-23}\text{cm}^2$	$S_{J'}/10^{-21}\text{cm}^2$
⁴ I _{13/2}	1540.9	0.0191	0.1179	1.4309	11.3015	13.7713
⁴ I _{11/2}	986	0.0281	0.0002	0.3958	4.2636	4.7203
⁴ I _{9/2}	804.6	0	0.1738	0.0099	1.3174	1.5237
⁴ F _{9/2}	654.7	0	0.5353	0.4619	8.7108	10.3608
⁴ S _{3/2}	541	0	0	0.2211	1.0458	1.2745
² H _{11/2}	519	0.7124	0.4123	0.0925	9.4401	11.1739
⁴ F _{7/2}	488	0	0.1468	0.6266	5.3117	6.4948
⁴ F _{5/2}	452.45	0	0	0.2231	0.7425	0.8201
⁴ F _{3/2}	441.1	0	0	0.1272	1.2611	1.4214
² H _{9/2}	400.7	0	0.0190	0.2254	2.6321	2.8352
⁴ G _{11/2}	378.96	0.9182	0.5261	0.1171	15.1142	19.0383
⁴ G _{9/2}	368.2	0	0.2414	0.1234	2.1748	2.2831
² G _{7/2}	359.13	0	0.0173	0.1163	2.3047	2.4825

probability induced by the electric dipole moment transition can be expressed as follows:

$$A_{JJ'}^{ed} = \frac{16\pi^3 e^2 n(n^2 + 2)^2}{27(2J + 1)h\epsilon_0 \lambda^3} \sum_{\lambda} \Omega_{\lambda} \left| \langle aSLJ | U^{(\lambda)} | a'S'L'J' \rangle \right|^2 \quad (4)$$

where α, S, L, J and α', S', L', J' represent the quantum numbers of the initial state and terminal state, respectively.

The J-O theory can be used to evaluate the radiative properties of the rare-earth ions by using J-O parameters.

The fluorescence branch ratio $\beta_{JJ'}$, the fluorescence life τ and the integral emission cross-section can be expressed as follows: where $A_{JJ'}$ represents the probability of spontaneous ra

$$\beta_{JJ'} = \frac{A_{JJ'}}{\sum_{J'} A_{JJ'}} \quad (5)$$

$$\tau = \frac{1}{\sum_{J'} A_{JJ'}} \quad (6)$$

$$\int \sigma_{em}(v) dv = \frac{\lambda^2}{8\pi n^2 c} A_{JJ'} \quad (7)$$

diation transition from energy level J to J' . the calculation of the spontaneous radiative transition probability, fluorescence life, fluorescence branch ratio and integral

emission cross-section for partial energy levels of Er³⁺ ions are shown in **Table 3**. The results prove that the ⁴I_{13/2}→⁴I_{15/2} transition corresponds to a larger integral emission cross-section, a higher fluorescence branch ratio and a longer fluorescence life, and which is the essential condition for generating laser oscillation. The laser output for the ⁴I_{13/2}→⁴I_{15/2} transition waveband can be obtained at room temperature.

3.3. Fluorescence Spectrum

The fluorescence spectra ranging from 900 to 1700 nm at room temperature were obtained under the 532 nm pumping shown in **Figure 2**. The main peak around 1530.5 nm is due to the Er³⁺ 4I_{13/2}→4I_{15/2} transition. From **Figure 2**, we can see that the FWHM of the sample is about 52 nm. It is well known that the broad emission band is fit for tunable laser medium. Therefore, the fluorescence spectra indicates that Er:LiGdF₄ crystal is a potential candidate for compact and efficient near-infrared lasers.

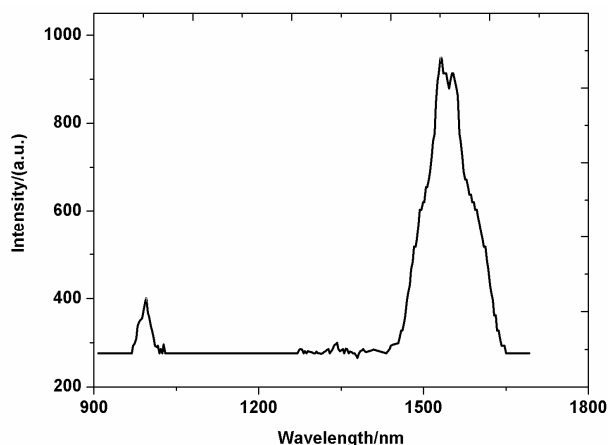
The stimulate emission cross-sections were calculated by the Fuchtbauer-Ladenburg (F-L) equation [20]:

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

where c is the speed of light, n is the refractive index, η is the radiative efficiency that can be estimated from the

Table 3. Spectral parameters of Er:LiGdF₄ crystal sample.

transition	$A_{J,J'}/s^{-1}$	$B_{J,J'}$	τ/ms	$\int \sigma_{em}(\nu) d\nu/10^{-18} cm^2$
$^4I_{13/2} \rightarrow ^4I_{15/2}$	222.2123	1	4.5002	1.7137
$^4I_{11/2} \rightarrow ^4I_{13/2}$	36.9014	0.2049	3.9614	1.1246
$^4I_{9/2} \rightarrow ^4I_{11/2}$	3.0362	0.013	2.9431	0.312
$^4F_{9/2} \rightarrow ^4I_{9/2}$	168.7002	0.0854	0.3438	7.9909
$^4S_{3/2} \rightarrow ^4I_{9/2}$	75.7212	0.0377	0.3896	0.8362
$^2H_{11/2} \rightarrow ^4F_{9/2}$	10.6593	0.0013	0.1212	0.319
$^4F_{7/2} \rightarrow ^4F_{9/2}$	32.2013	0.0068	0.2018	0.4921

**Figure 2. Photoluminescence spectrum of Er:LiGdF₄ crystal Excited by 532 nm laser.**

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. (8), the Er³⁺ $4I_{13/2} \rightarrow 4I_{15/2}$ IR transition is a broad emission band at about 1530.5 nm. The corresponding FWHM is 52 nm, and the maximum emission cross-section of the Er³⁺ $4I_{13/2} \rightarrow 4I_{15/2}$ transition is $2.127 \times 10^{-20} cm^2$ near 1530.5 nm.

4. Conclusions

Er³⁺-doped LiGdF₄ single crystal was grown successfully by Czochralski method. The absorption spectrum was measured at room temperature. The broad absorption band and relative high absorption cross-section around 986 and 1540.9 nm are suitable for laser diode pumping. The Judd-Ofelt theory has been applied to the analysis of the room temperature absorption spectrum. Three intensity parameters were obtained: $\Omega_2 = 0.905 \times 10^{-20} cm^2$, $\Omega_4 = 2.47 \times 10^{-20} cm^2$ and $\Omega_6 = 4.92 \times 10^{-20} cm^2$. The room temperature emission spectra were recorded. The Er³⁺ $4I_{13/2} \rightarrow 4I_{15/2}$ IR transition is a broad emission band at about 1530.5 nm; the corresponding FWHM is 52 nm. The stimulated emission cross-section around 1530.5 nm were calculated by the F-L equation. The maximum emission cross-section with the peak at 1530.5 nm is $2.127 \times 10^{-20} cm^2$.

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