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Optical Characterization of Erbium Doped KY_3F_{10} Fluoride Single Crystals

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ABSTRACT

Preparation and optical characterisation of Erbium doped KY_3F_{10} single crystals are reported. The crystals were grown using the Czochralski pulling technique. The single phase was controlled by X-ray diffraction analysis. Room temperature optical spectra were recorded between 200 and 1600 nm. They were used to fit the three phenomenological Judd-Ofelt (JO) parameters Ω_t ($t = 2, 4, 6$). The emission transition probabilities, branching ratios and radiative lifetimes are then deduced. The possibility to use such material for laser emissions is discussed.

Keywords: Solid State Laser; Laser Spectroscopy; Laser Materials; Fluoride; Rare Earth; KY_3F_{10} Crystals; Judd-Ofelt Theory

1. Introduction

The fluoride single crystals were intensively studied during the last decade [1-8] in order to develop efficient and reliable all solid state lasers emitting in both visible and near infrared domain. The crystals studied are doped with rare earth ions which constitute the optically active centres by considering the 4f-4f transitions. Among all solid-state laser materials, the fluorides have the advantageous to be transparent in a large electromagnetic domain and they have low-maximum phonon frequency leading to a large number of potential emitting levels.

In this study, we present the optical absorption properties of KY_3F_{10} laser material doped with trivalent Erbium ions. The Judd-Ofelt (JO) analysis was applied to this crystal in order to determine the optical transition probabilities, the branching ratio and the radiation lifetimes of the Erbium main emitting levels. The study seems to have not been done previously as far as we know. It enriches the literature and shows that the investigated crystal offers the possibility to generate a lot of emissions in the near infrared spectral range and especially the visible range.

2. Experimental Procedure

2.1. Material

The KY_3F_{10} compound belongs to KF-YF_3 pseudo-binary system. It melts congruently with a not very high melting point [9]. It crystallises in a face centred cubic structure having eight molecules per unit cell. The lattice is made up of two ionic groups $(KY_3F_8)^{2+}$ and $(KY_3F_{12})^{2-}$ which are alterned along orthogonal crystallographic directions [10,11]. All atoms occupy special crystallographic positions. Potassium and Yttrium ions are placed at 8c and 24e Wyckoff sites respectively. Fluorine ions occupy two different sites [12]. The Yttrium ions, for which are partially substituted the Er^{3+} ions, occupy a C_{4v} tetragonal symmetry site. KY_3F_{10} is an isotropic crystal.

2.2. Growth and Optical Techniques

Crystals of KY_3F_{10} doped with different concentrations of Erbium ions were grown by Czochralski technique. We use three fluoride compounds: KF, YF_3 and ErF_3. These powder compounds with 4N (99.99%) purity are from Merck an Aldrich. They are finely crushed and weighed in the stoichiometric proportions and placed in a vitreous carbon crucible. We, first, heat the mixture under vacuum for 4 h with progressive temperature increase until 500˚C. Czochralski pulling takes place with a molybdenum rod under continuous argon circulation highly purified. The pulled crystals have more than 1 cm in diameter and 3 cm in length. Checked in polarized light, they are exempted of makles, crackles. They could be easily cut into laser bulk single crystals with high optical quality. The sample used for optical absorption measurements was polished to flat and parallel faces.

X-ray diffraction spectra confirm that KY_3F_{10} single crystals have a cubic structure with a lattice parameter a

= 11.55 Å in good agreement with literature data [9,12, 13]. The Erbium ions which substitute Yttrium ions occupy C_{4v} symmetry sites. The pulled crystals are of good optical quality. For spectroscopic measurements, the crystals were cleaved and polished in order to obtain parallel face samples with 2.65 mm thickness. The room temperature optical spectra were recorded with a Perkin-Elmer Lambda 9 double beam spectrophotometer. As KY_3F_{10} is an isotropic crystal, the absorption spectra were obtained without using the birefringent polarizer of the used spectrophotometer.

3. Optical Spectroscopy

3.1. Judd-Ofelt Theory

In Judd-Ofelt approach [14,15], the measured electric dipole transition strengths $\left(S_{JJ'}^{DE}\right)^{\text{meas}}$ of the chosen transition $\left(J \to J'\right)$ are determined using the following expression:

$$\left(S_{JJ'}^{DE}\right)^{\text{meas}} = \frac{9 \cdot n}{\left(n^2+2\right)^2}\left[\frac{3 \cdot h \cdot c \cdot \left(2 \cdot J+1\right) \cdot \varepsilon_0}{2 \cdot \pi^2 \cdot e^2 \cdot \bar{\lambda}} \cdot \frac{\ln 10}{N \cdot L}\int_{J \to J'} DO\left(\lambda\right) \cdot \mathrm{d}\lambda - n \cdot S_{JJ'}^{DM}\right] \quad (1)$$

Where J and J' represent the total angular momentum quantum numbers of the initial and final levels, respectively, n the refractive index of the material, h the Planck constant, c the vacuum light celerity, ε_0 the vacuum permittivity, e the electron charge, λ is the average wavelength of the $J \to J'$ absorption transition, N the Er^{3+} concentration, L the thickness of the sample, $DO(\lambda)$ the measured optical density and $S_{JJ'}^{DM}$ is the magnetic dipolar line strengths.

In the case of Er^{3+}, many transitions have magnetic dipolar components [16].

The three J-O intensity parameters Ω_2, Ω_4 and Ω_6 can be then calculated by solving the over determined set of equation given by the following equation:

$$\left(S_{JJ'}^{DE}\right)^{\text{cal}} = \sum_{t=2,4,6} \Omega_t \left|\left\langle \left\| U^{(t)} \right\| \right\rangle\right|^2 \quad (2)$$

Where $\left|\left\langle \left\| U^{(t)} \right\| \right\rangle\right|^2$ are the squared reduced matrix elements of rank t (t = 2, 4, 6) between the two multiplets characterized by the quantum number (S, L, J) and (S', L', J'). The matrix elements $U^{(t)}$ used in the present work were tabulated by Kaminski [17] for the Er^{3+} ions. However, when two absorption transitions are overlapped, the squared matrix element was taken to be the sum of the corresponding squared matrix elements.

Thus, a series of calculation was carried out while varying the number of transitions used in the fitting procedure. The fitting accuracy of each calculation was evaluated from the root mean-square (rms) deviation between measured and calculated line strengths of the transitions.

$$rms = \sqrt{\frac{\sum\left(\left(S_{JJ'}^{DE}\right)^{\text{cal}} - \left(S_{JJ'}^{DE}\right)^{\text{meas}}\right)^2}{q-3}} \quad (3)$$

Where q is the number of spectral bands analyzed and 3 reflects the number of fitting parameters.

The J-O parameters are determined from the fitting procedure and they are used to calculate other transitions properties between ground and excited states of the Er^{3+} ion.

The radiative transition probabilities $A_{JJ'}$ for emissions from emitting levels [$LS(J)$] are given by [16]:

$$A_{JJ'}^{\text{rad}} = \frac{64\pi^3 e^2}{3h\bar{\lambda}^3\left(2J+1\right)}\left[\frac{n\left(n^2+2\right)^2}{9} S^{DE} + n^3 S^{MD}\right] \quad (4)$$

Where the electric dipole line strengths (S^{DE}) are calculated from Equation (2) while the magnetic dipole line strengths used in this work are reported in [16,18]. Then, the radiative lifetime τ for an excited state (J) is calculated by:

$$\tau_R = \frac{1}{\sum_{J'} A_{JJ'}} \quad (5)$$

Where the summation of $A_{JJ'}$ terms is over all lower energy levels. The branching ratio β_R is given by the equation:

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

3.2. Data Analysis and Results

Room temperature optical spectra were recorded between 200 and 1600 nm. The observed spectra were independent of doping concentration in the range 0.1% - 1% molar concentration. **Figure 1** shows the erbium energy levels.

The Judd-Ofelt theory, widely used to analyse the forced electric dipole transitions within the $4f^n$ configuration of the rare earth ions and extensively introduced in the literature [19-23] is performed on Er^{3+} doped KY_3F_{10}. We have identified seven absorption bands around 518.85 nm, 553.86 nm, 574.35 nm, 685.28 nm, 829.31 nm, 973.26 nm and 1521.65 nm (**Figure 2**).

The observed bands are attributed, respectively, to the multiplets $^4F_{7/2}$, $^2H_{11/2}$, $^4S_{3/2}$, $^4F_{9/2}$, $^4I_{9/2}$, $^4I_{11/2}$ and $^4I_{13/2}$ [5]. They are used in the fitting procedure. The three phenomenological obtained parameters, by the method of least-square fitting, are Ω_2 = 1.932, Ω_4 = 0.729 and Ω_6 =

1.953 with *rms* = 0.345 (in 10^{-20} cm^2·units). These parameters are in accordance with those calculated for other fluoride hosts [24-28]. The spectroscopic quality factor $\chi = \Omega_4/\Omega_6$ is approximately 0.37 which is in the range of 0.11 - 1.25. The calculated $\left(S_{JJ'}^{DE}\right)^{cal}$ line strengths for all measured transitions were then deduced (**Table 1**). The computed transition probabilities and corresponding radiative lifetimes were then deduced and are given in **Table 2**.

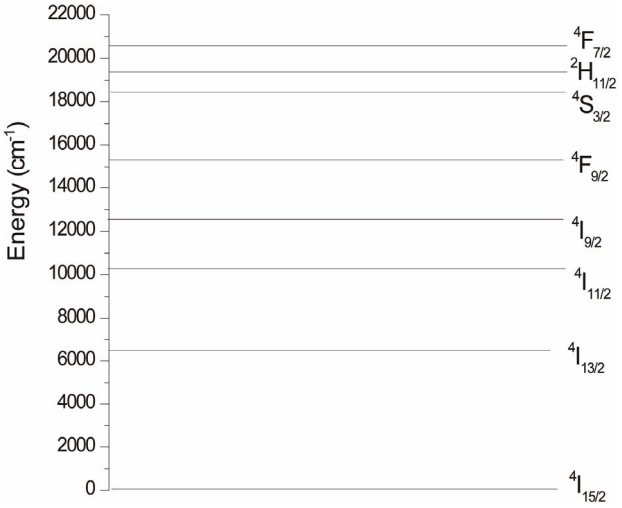

Figure 1. Energy level scheme of Erbium.

It is obvious that the branching ratio and the radiative lifetime are two critical parameters that can predict the possibility of laser emission. In the case of the infrared transition whose emission wavelength is centered around 1521 nm, the branching ratio is maximum and the radiative lifetime is nearly equal to 7 ms. Such a transition is investigated for eye safe laser. The level $^4I_{13/2}$ is metastable level which may serve as reservoir level. The KY_3F_{10} compound is serious contenders for eye-safe near infrared laser systems that can be efficiently pumped at 980 nm emitted by commercialized diode laser. Also, the fluorescence branching ratios for $^2H_{11/2} \rightarrow {}^4I_{15/2}$ and $^4S_{3/2} \rightarrow {}^4I_{15/2}$ transitions are 92% and 67% respectively which is large enough to be available to generate green light up-conversion emission. Therefore, Erbium doped KY_3F_{10} crystal may be regarded as a potential solid-state Er^{3+} laser host material.

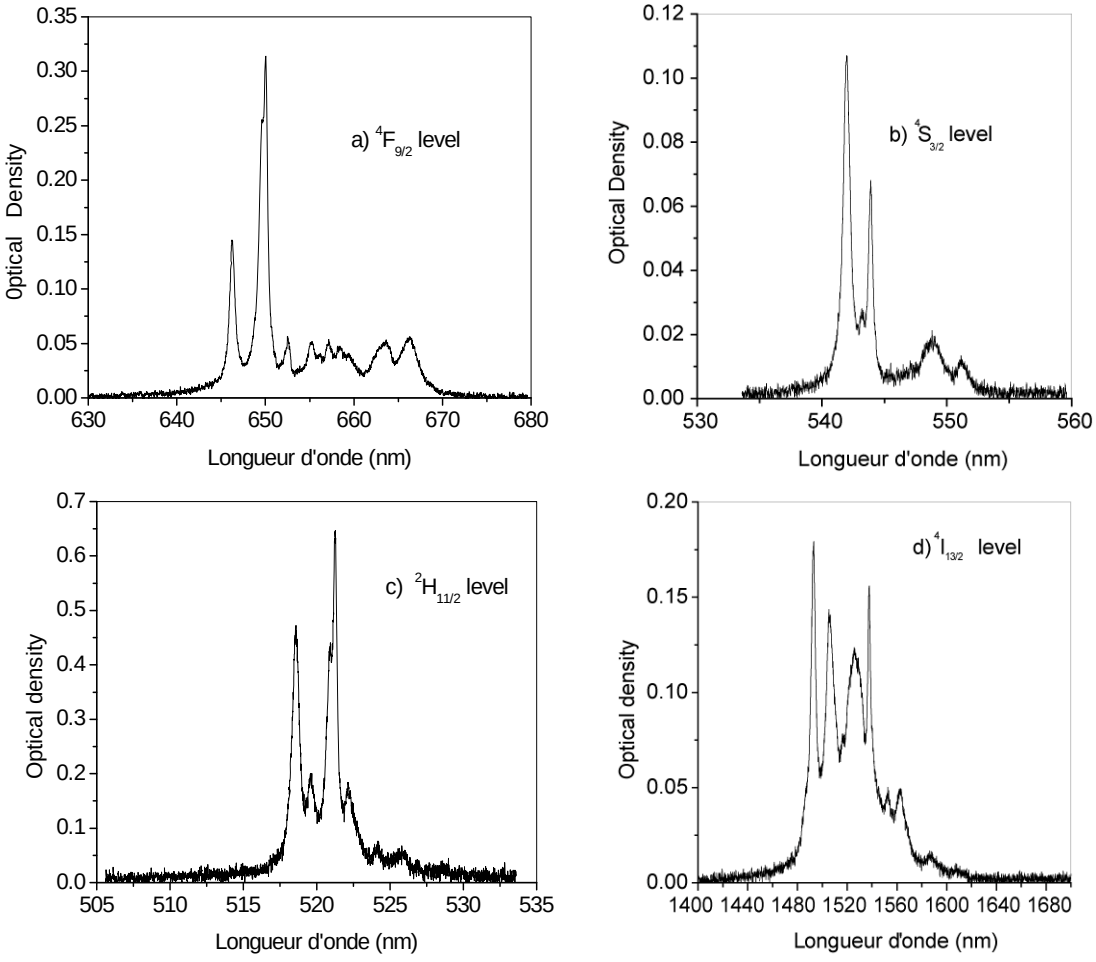

Figure 2. Room temperature absorption spectra of Er^{3+} doped KY_3F_{10}.

Table 1. Measured and calculated transition strengths for Er^{3+} ions in KY_3F_{10} single crystal.

Transition: $^4I_{15/2} \rightarrow$	λ (nm)	Energy (cm^{-1})	$S_{JJ'}^{DE\text{mes}}$ $(\times 10^{-20}\,cm^2)$	$S_{JJ'}^{DE\text{cal}}$ $(\times 10^{-20}\,cm^2)$
$^4I_{13/2}$	1521.65	6571.8	2.88	2.92
$^4I_{11/2}$	973.3	10274.7	1.42	0.83
$^4I_{9/2}$	829.3	12058.2	0.22	0.15
$^4F_{9/2}$	685.3	14592.6	1.38	1.29
$^4S_{3/2}$	574.3	17411.0	0.30	0.43
$^2H(2)_{11/2}$	553.9	18055.1	1.83	1.86
$^4F_{7/2}$	518.8	19273.4	1.03	1.33

Table 2. Calculated electric and magnetic dipole emission probabilities, life times and branching ratios in KY_3F_{10} doped with Erbium ions.

Transition	Average wavelength λ (nm)	A^{DE} (s^{-1})	A^{DM} (s^{-1})	β (%)	τ_{rad} (ms)
$^4I_{13/2} \rightarrow {}^4I_{15/2}$	1521.65	121.37	32.94	100	6.48
$^4I_{11/2} \rightarrow {}^4I_{15/2}$	973.26	153.26	0	85	5.53
$^4I_{13/2}$	2700.51	20.05	7.66	15	
$^4I_{9/2} \rightarrow {}^4I_{15/2}$	829.31	52.35	0	52	9.91
$^4I_{13/2}$	1822.82	47.65	0	47	
$^4I_{11/2}$	5608.52	0.35	0.54	1	
$^4F_{9/2} \rightarrow {}^4I_{15/2}$	685.28	832.93	0	91.40	1.098
$^4I_{13/2}$	1246.72	28.65	0	3.10	
$^4I_{11/2}$	2315.88	43.78	3.17	5.20	
$^4I_{9/2}$	3944.77	1.02	1.56	0.30	
$^4S_{3/2} \rightarrow {}^4I_{15/2}$	574.35	1169.00	0	69.50	0.595
$^4I_{13/2}$	922.59	441.45	0	26.30	
$^4I_{11/2}$	1401.34	27.46	0	1.60	
$^4I_{9/2}$	1868.11	43.56	0	2.60	
$^4F_{9/2}$	3548.61	0.59	0	0.00	
$^2H_{11/2} \rightarrow {}^4I_{15/2}$	553.86	1869.00	0	92.40	0.494
$^4I_{13/2}$	870.85	49.66	38.57	4.40	
$^4I_{11/2}$	1285.34	19.49	4.31	1.20	
$^4I_{9/2}$	1667.50	37.15	0.38	1.90	
$^4F_{9/2}$	2888.50	5.12	0.08	0.10	
$^4S_{3/2}$	15527.95	0.00	0	0	
$^4F_{7/2} \rightarrow {}^4I_{15/2}$	518.85	2442.00	0	88.10	0.361
$^4I_{13/2}$	787.33	129.19	0	4.70	
$^4I_{11/2}$	1111.35	92.58	0	3.30	
$^4I_{9/2}$	1386.00	90.16	6.79	3.56	
$^4F_{9/2}$	2136.75	2.04	7.24	0.34	
$^4S_{3/2}$	5370.56	0.00	0	0	
$^2H_{11/2}$	82.10.18	0.48	0	0	

4. Conclusion

Er^{3+} doped single crystals were grown by Czochralski technique. The measured absorption line strengths at room temperature were used for a standard Judd-Ofelt analysis. The JO parameters were determined and they are in accordance with those calculated for other fluorid hosts. The radiative transition probabilities, radiative lifetimes and branching ratios of the main intermanifold transitions of Er^{3+} were calculated. Because of his low phonon energies, this crystal could permit up-conversion laser emissions. This study shows that Er^{3+} doped KY_3F_{10} crystal possesses several competitive spectroscopic properties suggesting that this material can give rise to laser emissions in the near infrared spectral range (in the case of infrared transition $^4I_{13/2} \rightarrow {}^4I_{15/2}$) as well as in the visible (for the green transition $^2H_{11/2}$, $^4S_{3/2} \rightarrow {}^4I_{15/2}$).

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