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# JUDD-OFELT ANALYSIS OF THE $Er^{3+}$ IONS IN $CaF_2$ CRYSTALS

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**Abstract**
Calcium fluoride is a well-known crystal that can be grown easily by Bridgman or Czochralski techniques; $CaF_2$ crystals has been used for long time in many optical components due to its exceptional transparency in the UV as well as in the IR. In this work a Judd-Ofelt investigation on the $Er^{3+}$ ions in $CaF_2$:$ErF_3$ single crystals with various $ErF_3$ concentrations have been performed. The intensity parameters are used to determine the emission probabilities of transitions and the branching ratios of the $Er^{3+}$ transitions. The radiative life times of the excited states are also determined.
**Keywords**: Judd-Ofelt theory, intensity parameters, absorption spectrum, reduced matrix operator.

## 1. Introduction

The $CaF_2$ crystals have been used for long time in many optical components due to its exceptional transparency in the UV as well as in the IR spectral domain. Due to their optical properties, $CaF_2$ appears as a very attractive laser host which combines several advantages of calcium fluoride crystals and glasses. Another interest of $CaF_2$:$Er^{+3}$ laser material, compared with other fluoride crystals resides in the possibility of the pumping with laser diodes and the choice of the excitation wavelength is not critical parameter because of the broad absorption bands. The optical properties of $CaF_2$ doped with trivalent rare-earth (RE) ions have been investigated by many authors [1,2,3]. In order to characterize the laser properties of these compounds we can use experimental or theoretical techniques.

The Judd-Ofelt model [4,5] permits to calculate some characteristics of the stimulated emission only from the absorption spectra [1,2,3]. In this paper we report a study about the influence of $Er^{3+}$ ions concentration on the optical absorption spectra as well as the usage the Judd-Ofelt model in order to determine the intensity parameters $\Omega_i$ and the study the influence of the $Er^{3+}$ ion concentration on the $\Omega_i$ parameters.

## 2. Experimental procedure

Pure and $ErF_3$ – doped $CaF_2$ crystals have been grown in vacuum ($10^{-1}$Pa) in our crystal research laboratory using vertical Bridgman method [6]. A chemically pure grade (99,9%) $ErF_3$ reagent and suprapure grade Merck calcium fluoride were used as the starting materials. Transparent single crystals with various concentrations (0.15, 0.30 and 0.67 mol% $ErF_3$) in graphite crucible have been obtained. The rate of the crucible lowering was 4 mm/h.

The optical absorption spectra at room temperature have been obtained using a Shimadzu 1650PC spectrophotometer.

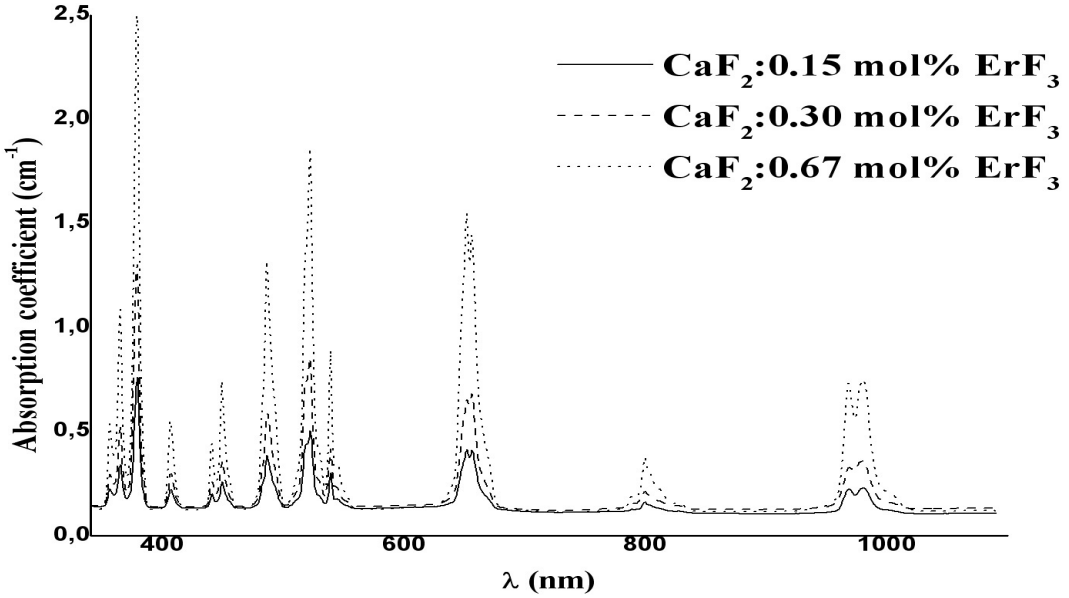


*Fig. 1: Absorption spectra of various $ErF_3$ concentrations doped $CaF_2$ crystals.*

## 3. Results and Discussions

In order to characterize the laser properties of laser materials we can use experimental or theoretical techniques. To investigate the stimulated emission some parameters must be known: the probability of the spontaneous emission ($A_{JJ'}$) and of the nonradiative transitions ($W_{JJ'}$), for example. Probability $A_{JJ'}$ is the sum of the probabilities of forced electric-dipole (ed) and magnetic-dipole (md) transitions; these parameters can be calculated if we known the line strength $s_{JJ}^{ed}$ and $s_{JJ}^{md}$. In these expressions the $\Omega_t$ parameters appears, which are the intensity parameters describing the efficiency of the interaction between the $RE^{3+}$ activator

ion and the surrounding crystal field. The Judd-Ofelt model [4, 5] permits to calculate these parameters from the investigation of the absorption spectra only.

The Judd-Ofelt model can be applied to the analysis of the absorption intensities of RE ($4f^N$) transitions in the rare-earth-doped crystals, in order to determine the intensity parameters $\Omega_2$, $\Omega_4$, $\Omega_6$. Electric and magnetic dipole transitions between levels of the $4f^N$ configurations are perturbed by the static crystalline field.

The oscilator strength $S_{\text{calc}}^{\text{el}}$ corresponding to the electric dipole transition from the ground level $\Psi'_{\text{J}'}$ is given by [1]:

$$S_{\text{calc}}^{\text{el}} = \sum_{t=2,4,6} \Omega_t \left| \left\langle \Psi_{\text{J}} \left\| U^{(t)} \right\| \Psi'_{\text{J}'} \right\rangle \right|^2$$

where $U^{(t)}$ is a tensor operator of rank $t$ ($t$ = 2,4,6), and $\Omega_t$ are the so-called Judd-Ofelt parameters or intensity parameters.

Ten $Er^{3+}$ absorption bands in the room-temperature absorption spectrum between 350 and 1000 nm (shown in Fig. 1), were chosen to determine Judd-Ofelt intensity parameters for $Er^{3+}$ in $CaF_2$ for three different $Er^{3+}$ concentrations: 0.15, 0.30 and 0.67 mol% $ErF_3$. The peak wavelengths of the $Er^{3+}$ bands are given in Table 1. The measured line strengths $\left(S_{\text{JJ}'}^{\text{ed}}\right)_{\text{meas.}}$ of the chosen bands are determined using the following expression [1,3]:

$$\left(S_{\text{JJ}'}^{\text{ed}}\right)_{\text{meas.}} = \frac{1}{N_0} \int k(\lambda) \mathrm{d}\lambda \frac{3 \cdot hc(2J+1)}{8\pi^3 e^2 \bar{\lambda}} \cdot \frac{9 \cdot n}{(n^2+2)^2} \tag{1}$$

where $J$ and $J'$ are the total angular momentum quantum numbers of the initial and final states, respectively, $n$ is the refractive index, $N_0$ is the $Er^{3+}$ ion concentration, $\bar{\lambda}$ is the mean wavelength of the specific absorption band and $\int k(\lambda)\mathrm{d}\lambda$ is the integral of the absorption coefficient of the band associated with the transition $\text{J} \rightarrow \text{J}'$. The refractive indices of CaF2:$Er^{3+}$ for all erbium concentrations was determined from Sellmeier's dispersion equation:

$$n(\bar{\lambda}_{\text{JJ}'}) = \sqrt{1 + \frac{B_1 \bar{\lambda}_{\text{JJ}'}^2}{\bar{\lambda}_{\text{JJ}'}^2 - C_1} + \frac{B_2 \bar{\lambda}_{\text{JJ}'}^2}{\bar{\lambda}_{\text{JJ}'}^2 - C_2} + \frac{B_3 \bar{\lambda}_{\text{JJ}'}^2}{\bar{\lambda}_{\text{JJ}'}^2 - C_3}} \tag{2}$$

where $B_i$ and $C_i$ $(i = 1,2,3)$ are Sellmeier's coefficients: $B_1 = 5.675888 \times 10^{-1}$, $B_2 = 4.710914 \times 10^{-1}$, $B_3 = 3.8484723$, $C_1 = 2.52642999 \times 10^{-3}$, $C_2 = 1.00783328 \times 10^{-2}$ and $C_3 = 1.20055597 \times 10^{3}$.

*Table 1: Values of reduced matrix elements for the absorption bands of $Er^{3+}$ in $CaF_2$ [1]*

| Transition from $^4I_{15/2}$ | $\bar{\lambda}$ (nm) | $n$ | $\left[U^{(2)}\right]^2$ | $\left[U^{(4)}\right]^2$ | $\left[U^{(6)}\right]^2$ |
|---|---|---|---|---|---|
| $^4I_{11/2}$ | 977 | 1.429 | 0.0282 | 0.0003 | 0.3953 |
| $^4I_{9/2}$ | 805 | 1.430 | 0 | 0.1732 | 0.0099 |
| $^4F_{9/2}$ | 655 | 1.432 | 0 | 0.5354 | 0.4619 |
| $^4S_{3/2}$ | 545 | 1.435 | 0 | 0 | 0.2211 |
| $^2H(2)_{11/2}$ | 519 | 1.436 | 0.7125 | 0.4123 | 0.0925 |
| $^4F_{7/2}$ | 487 | 1.437 | 0 | 0.1468 | 0.6266 |
| $^4F_{5/2}$ | 447 | 1.439 | 0 | 0 | 0.2233 |
| $^2G(1)_{9/2}$ | 406 | 1.441 | 0 | 0.0190 | 0.2255 |
| $^4G_{11/2}$ | 379 | 1.444 | 0.9181 | 0.5261 | 0.1171 |
| $^4G_{9/2}$ | 360 | 1.445 | 0 | 0.2415 | 0.1234 |

The measured line strengths were used to obtain the Judd-Ofelt parameters $\Omega_2$, $\Omega_4$ and $\Omega_6$ by solving a set of ten equations simultaneously for the corresponding transitions between $J$ and $J'$ manifolds in the following form:

$$\left(S_{JJ'}^{ed}\right)_{calc.} = \sum_{t=2,4,6} \Omega_t \left|\left\langle 4f^n \alpha[L,S]J \left\| U^{(t)} \right\| 4f^n \alpha'[L',S']J' \right\rangle\right|^2 \tag{3}$$

where $\left\langle \left\| U^{(t)} \right\| \right\rangle$ are the doubly reduced matrix elements of rank $t$ ($t = 2,4,6$) between states characterized by the quantum numbers $(S, L, J)$ and $(S', L', J')$. The values of the reduced matrix elements are given in Table 1 and the values of the measured and calculated absorption line strengths are given in Table 2. The values of the J-O parameters calculated for three different erbium concentrations are give in Table 3. The J-O parameters can now be applied to calculate, using equation (3), the line strengths, corresponding to the transition from the upper manifold states, $^4I_{11/2}$, $^4I_{9/2}$, $^4F_{9/2}$, $^4S_{3/2}$, $^2H(2)_{11/2}$, $^4F_{7/2}$, $^4F_{5/2}$ and $^2G(1)_{9/2}$ to their corresponding lower-lying manifolds states. Using these line strengths, the radiative decay rates, $A_{JJ'}$, for electric dipole transitions between an excited states (J) and the lower-lying terminal manifolds (J') can be calculated using the expression [1]:

$$A_{JJ'} = \frac{16\pi^3 e^2}{3h(2J+1)} \frac{n(n^2+2)^2}{9} \left(S_{JJ'}^{ed}\right)_{calc.} \tag{4}$$

*Table 2: Measured and calculated absorption line strengths of $Er^{3+}$ in $CaF_2$.*

| Concentration of $Er^{3+}$ | 0.15 mol% | | 0.30 mol% | | 0.67 mol% | |
|---|---|---|---|---|---|---|
| Transition from $^4I_{15/2}$ | $\left(S^{ed}_{JJ'}\right)_{meas.}$ $\times 10^{-20}\,cm^2$ | $\left(S^{ed}_{JJ'}\right)_{calc.}$ $\times 10^{-20}\,cm^2$ | $\left(S^{ed}_{JJ'}\right)_{meas.}$ $\times 10^{-20}\,cm^2$ | $\left(S^{ed}_{JJ'}\right)_{calc.}$ $\times 10^{-20}\,cm^2$ | $\left(S^{ed}_{JJ'}\right)_{meas.}$ $\times 10^{-20}\,cm^2$ | $\left(S^{ed}_{JJ'}\right)_{calc.}$ $\times 10^{-20}\,cm^2$ |
| $^4I_{11/2}$ | 1.19484 | 1.02122 | 1.11966 | 0.92318 | 1.32161 | 1.06635 |
| $^4I_{9/2}$ | 0.37849 | 0.44941 | 0.34634 | 0.42192 | 0.41429 | 0.47651 |
| $^4F_{9/2}$ | 2.44823 | 2.45268 | 2.24506 | 2.26101 | 2.59892 | 2.59826 |
| $^4S_{3/2}$ | 0.47097 | 0.54517 | 0.35545 | 0.49048 | 0.48819 | 0.57685 |
| $^2H(2)_{11/2}$ | 2.30644 | 2.39657 | 2.21259 | 2.30857 | 2.21233 | 2.17921 |
| $^4F_{7/2}$ | 1.73245 | 1.90524 | 1.56423 | 1.72902 | 1.79117 | 2.01678 |
| $^4F_{5/2}$ | 0.87597 | 0.55059 | 0.80683 | 0.49536 | 0.91134 | 0.58259 |
| $^2G(1)_{9/2}$ | 0.43984 | 0.60624 | 0.39568 | 0.54412 | 0.46899 | 0.63777 |
| $^4G_{11/2}$ | 3.13488 | 3.07027 | 3.02660 | 2.95814 | 2.75558 | 2.78912 |
| $^4G_{9/2}$ | 1.08832 | 0.89686 | 1.02737 | 0.83142 | 1.16015 | 0.95036 |

Table 3: J-O parameters for various $ErF_3$ concentrations in $CaF_2$ crystals.

| Concentration of $Er^{3+}$ | $\Omega_2$ $\times 10^{-20}\,cm^2$ | $\Omega_4$ $\times 10^{-20}\,cm^2$ | $\Omega_6$ $\times 10^{-20}\,cm^2$ |
|---|---|---|---|
| 0.15 mol% | 1.62356 | 2.45380 | 2.46572 |
| 0.30 mol% | 1.61584 | 2.30920 | 2.21837 |
| 0.65 mol% | 1.21408 | 2.60210 | 2.60899 |

The radiative lifetime, $\tau_{rad}$, for an excited state is:

$$\tau_{rad.} = \frac{1}{\sum_{J'} A_{JJ'}} \tag{5}$$

where the sum is taken over all final lower-lying states *J'*. The fluorescence branching ratios, $\beta_{JJ'}$, can be determined from the radiative decay rates by the following expression:

$$\beta_{JJ'} = \frac{A_{JJ'}}{\sum_{J'} A_{JJ'}} = A_{JJ'}\tau_{rad.} \tag{6}$$

All these values are given in Table 4.

*Table 4: Predicted probability of spontaneous emission, branching ratios and radiative lifetimes of $CaF_2:Er^{+3}$.*

| Transition from $^4I_{15/2}$ | 0.15 mol% | | | 0.30 mol% | | | 0.67 mol% | | |
|---|---|---|---|---|---|---|---|---|---|
| | $A_{JJ'}$ ($s^{-1}$) | $\beta_{JJ'}$ | $\tau_{rad}$ (ms) | $A_{JJ'}$ ($s^{-1}$) | $\beta_{JJ'}$ | $\tau_{rad}$ (ms) | $A_{JJ'}$ ($s^{-1}$) | $\beta_{JJ'}$ | $\tau_{rad}$ (ms) |
| $^4I_{11/2}$ | 171.294 | 0.855 | 4.99 | 154.849 | 0.852 | 5.506 | 178.868 | 0.856 | 4.786 |
| $^4I_{9/2}$ | 162.205 | 0.713 | 4.398 | 152.282 | 0.721 | 4.738 | 171.987 | 0.714 | 4.151 |
| $^4F_{9/2}$ | 1650.30 | 0.913 | 0.553 | 1521.342 | 0.913 | 0.600 | 1748.262 | 0.914 | 0.523 |
| $^4S_{3/2}$ | 1600.34 | 0.665 | 0.415 | 1439.810 | 0.664 | 0.461 | 1693.343 | 0.665 | 0.392 |
| $^2H(2)_{11/2}$ | 2720.14 | 0.906 | 0.333 | 2620.266 | 0.908 | 0.346 | 2473.441 | 0.898 | 0.363 |
| $^4F_{7/2}$ | 3935.98 | 0.8053 | 0.204 | 3571.948 | 0.8010 | 0.22425 | 4166.434 | 0.8055 | 0.1933 |
| $^4F_{5/2}$ | 1969.05 | 0.5104 | 0.2592 | 10629.185 | 0.5059 | 0.04760 | 12500.84 | 0.5104 | 0.0408 |
| $^2G(1)_{9/2}$ | 1735.05 | 0.5105 | 0.2942 | 1566.554 | 0.5060 | 0.32303 | 1822.406 | 0.5170 | 0.2837 |

## 4. Conclusions

A spectroscopic Judd-Ofelt study has been performed on $ErF_3$-doped $CaF_2$ crystals in order to investigate its potential as a laser material. The intensity parameters $\Omega_t$ have been calculated from absorption spectra taken at room-temperature. The radiative decay rates and the radiative lifetimes for three various concentrations have been calculated.

The higest value of radiative decay rates has been obtained for 0.67 mol% $ErF_3$ for transition $^4I_{15/2} \rightarrow {}^4F_{5/2}$.

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