

Judd–Ofelt analysis of powder samples: LiNbO₃:Er³⁺ submicron-sized particles as a model case



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ABSTRACT

In this work, a modified procedure for Judd–Ofelt analysis in powder samples is presented. The strength of this method lies in the use of relative optical absorption spectra in terms of optical densities, without the need to quantify the sample thickness which, for powder samples, can be challenging. The method is valid for samples of arbitrary ion concentration and not restricted to diluted materials. Also, while applied here to Er³⁺ ions, the method is generic and it should be easily adapted to other lanthanide ions.

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1. Introduction

At present there is a renewed interest in the optical characterization of Rare-Earth (RE) doped micro- and nano-structured materials in connection with their potential applications in biomedical sciences, particularly for imaging and biodetection assays both in vitro and in vivo [1–4].

The theory formulated by Judd [5] and Ofelt [6] has been extensively used to determine the basic spectroscopic properties of RE-doped materials and it is considered a fundamental stage in the characterization of any luminescent material [7]. The fundamental idea is to use an absorption spectrum, with known absolute absorption cross sections, to quantify the three Judd–Ofelt (JO) intensity parameters, Ω_t ($t = 2, 4, 6$), adequate to describe the intensity of induced electric dipole transitions.

Unfortunately in powder samples the application of such analysis faces great difficulties, as has been pointed out elsewhere [8,9]. Possibly for that reason, quantitative studies of micro- and nano-structured materials for biological applications in the literature are scarce.

In this work an alternative JO procedure with applicability to powder samples is presented. The method is based on the use of relative (non-calibrated) optical absorption spectra and the subsequent calibration of transition probabilities through the use of a radiative lifetime. As a model case, we present the case of Er³⁺-doped LiNbO₃ submicron-sized powder samples which can

be compared with the analysis previously reported for bulk samples.

2. Experimental procedure

Submicron-sized Er³⁺-doped LiNbO₃ prepared by wet chemical synthesis [10] have been used. The particles were mounted in a specially designed holder constructed by using an aluminum foil spacer with a 10 mm × 5 mm rectangular opening, enclosed by two microscope slide covers, filling the cavity left in the aluminum which allows accurately measuring absorption spectra.

The optical absorption spectra were measured by using a Perkin Elmer Lambda 1050 spectrophotometer. Lifetime measurements were performed under excitation at 980 nm by using an infrared laser diode with intensity modulation capabilities. The luminescent signal was dispersed by using an ARC monochromator model SpectraPro 500-i and then detected synchronously with an InGaAs photodiode and recorded by a digital Tektronix TDS 420 oscilloscope.

3. Results and discussion

3.1. Calculation method

From the theoretical point of view, the oscillator strength, f_{cal} , associated to a $4f^N-4f^N$ optical transition can be evaluated through its electric-dipole and magnetic-dipole contributions by:

$$f_{cal}(J \rightarrow J') = \frac{8\pi^2 mc}{3h\lambda_m(2J+1)n^2} \left\{ \frac{n(n^2+2)^2}{9} S_{ed} + n^3 S_{md} \right\} \quad (1)$$

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where J and J' denote the initial and final manifolds, m the electron mass, c the speed of light, h Planck's constant, λ_m the barycentre wavelength for the $J \rightarrow J'$ absorption band, n the refractive index at λ_m and S_{ed} and S_{md} represent the electric-dipole and magnetic-dipole line strengths.

According to the JO theory, the electric-dipole line strength can be expressed in terms of the JO intensity parameters, Ω_t ($t = 2, 4, 6$), and the reduced matrix elements $|\langle \phi J || U^{(t)} || \phi' J' \rangle|^2$ as:

$$S_{ed}(J \rightarrow J') = \sum_{t=2,4,6} \Omega_t |\langle \phi J || U^{(t)} || \phi' J' \rangle|^2 \quad (2)$$

In general, the intensities of most RE optical transitions are of electric-dipole character, although some of them present also magnetic dipole character. The line strengths associated to these magnetic dipole transitions between $4f^n$ states are given by [11]:

$$S_{md} = \left(\frac{eh}{2mc} \right)^2 \times \left[\sum_{\alpha SL, \alpha' S' L'} C(\alpha SL) C(\alpha' S' L') \langle [\alpha SL] J || L + 2S || [\alpha' S' L'] J' \rangle \right]^2 \quad (3)$$

where $C(\alpha SL)$ is the intermediate coupling coefficient associated to the $[\alpha SL] J$ eigenstate. The matrix elements of the $(L + 2S)$ operator depend on ΔJ as follows:

$$\begin{aligned} \Delta J = 0 &\rightarrow \langle [\alpha SL] J || L + 2S || [\alpha' S' L'] J' \rangle \\ &= \delta(\alpha, \alpha') \delta(S, S') \delta(L, L') \times \left[\frac{2J+1}{4J(J+1)} \right]^{1/2} \\ &\quad \times [S(S+1) - L(L+1) + 3J(J+1)] \end{aligned} \quad (4)$$

$$\begin{aligned} \Delta J = -1 &\rightarrow \langle [\alpha SL] J || L + 2S || [\alpha' S' L'] J' \rangle \\ &= \delta(\alpha, \alpha') \delta(S, S') \delta(L, L') \\ &\quad \times \left[\frac{((S+L+1)^2 - J^2)(J^2 - (L-S)^2)}{4J} \right]^{1/2} \end{aligned} \quad (5)$$

$$\begin{aligned} \Delta J = 1 &\rightarrow \langle [\alpha SL] J || L + 2S || [\alpha' S' L'] J' \rangle \\ &= \delta(\alpha, \alpha') \delta(S, S') \delta(L, L') \\ &\quad \times \left[\frac{((S+L+1)^2 - (J+1)^2)((J+1)^2 - (L-S)^2)}{4(J+1)} \right]^{1/2} \end{aligned} \quad (6)$$

In the standard JO procedure, the theoretical oscillator strength values are compared with the measured magnitudes obtained from the optical absorption spectra, f_{mea} , that is, with the different oscillator strengths from the ground state manifold, J , to all the upper excited states, J' :

$$f_{mea}(J \rightarrow J') = \frac{2mc}{\alpha_f h N_T \lambda_m^2} \int_{band} \alpha(\lambda) d\lambda \quad (7)$$

where α_f is the fine-structure constant, N_T the active ion concentration and finally $\alpha(\lambda) = 2.3 \times O.D./d$ represents the absorption coefficient at wavelength λ . Comparing measured (f_{mea}) and calculated oscillator strengths (f_{cal}), and minimizing their differences, the Ω_t intensity parameters are obtained [12]. Therefore, the knowledge of ion concentration (N_T) and sample thickness (d) are needed. Such a procedure can be easily performed in bulk samples but it becomes challenging for powder samples which are normally handled in such a way that "thickness" is not a straightforward concept to be quantified accurately.

In order to overcome these difficulties, a modified procedure based on the use of excitation (rather than absorption) spectra and radiative decay rates, has been proposed [8]. Nevertheless, this

procedure relies on the proportionality between absorption and excitation spectra, and therefore it is strictly valid only for sufficiently low absorbance; that is for diluted materials.

In the present work, we propose an alternative analysis, valid for any RE concentration, following a two-step procedure:

- (1) A relative JO analysis is performed by using the absorption spectrum in terms of optical densities and,
- (2) the absolute JO parameters are calibrated by using a purely radiative lifetime.

In the first step, a relative line strength value is associated to each absorption band taking into account that, for purely electric-dipole transitions, line strengths and optical densities are related as:

$$S_{ed}^{mea}(J \rightarrow J') = \frac{9n}{(n^2 + 2)^2} \frac{C_{JO}}{\lambda_m} \int_{band} O.D.(\lambda) d\lambda \quad (8)$$

where C_{JO} is the proportionality coefficient relating the relative and absolute line strengths values. Then, these relative line strength values are used to calculate a set of three relative intensity parameters, ω_t , which are proportional to the absolute ones, Ω_t :

$$\Omega_t = C_{JO} \omega_t \quad (t = 2, 4, 6) \quad (9)$$

Then, the second step consists in the calibration of the relative intensity parameters (ω_t) by determining C_{JO} through the comparison of the calculated and measured lifetimes of a selected purely radiative transition. In order to illustrate the procedure, $\text{LiNbO}_3:\text{Er}^{3+}$ powders are analyzed next.

3.2. $\text{LiNbO}_3:\text{Er}^{3+}$ particles

Fig. 1 presents the absorption spectrum of the Er^{3+} -doped particles measured by using a Perkin Elmer Lambda 1050 spectrophotometer. The different absorption bands are identified with the optical transitions from the ground state, $^4I_{15/2}$, to the upper manifolds (labeled in the figure).

The inset shows the measured relative line-strengths ($S_{ed}^{rel} = S_{ed}^{mea}/C_{JO}$) together with the calculated ones from Eq. (2). The set of relative ω_t parameters have been obtained using a least-square algorithm to minimize the differences. The Er^{3+} reduced matrix elements and wavelength dependent refractive indices are taken from [13] and [14]. As usual in Er^{3+} -doped materials, the $^4I_{15/2} \rightarrow ^4F_{5/2}$ and $^4I_{15/2} \rightarrow ^4F_{3/2}$ absorption bands are overlapped and are treated as a single transition.

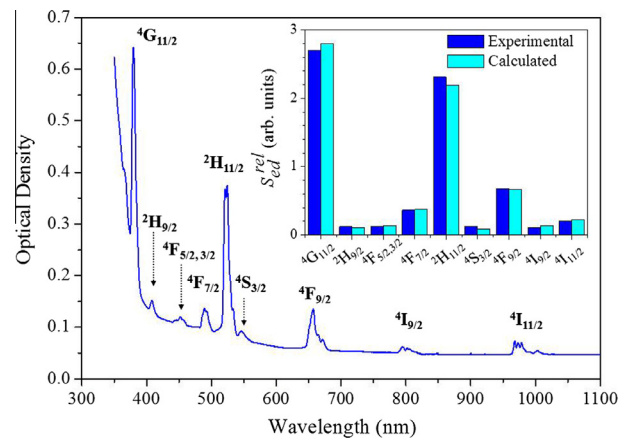


Fig. 1. Absorption spectrum of Er^{3+} -doped LiNbO_3 submicron-sized particles. The inset shows the relative values of the experimental and calculated electric dipole line strengths.

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