Spectroscopic properties of Er$^{3+}$ ions in LiNbO$_3$ crystals codoped with HfO$_2$

A. Li$^1$
L. Sun$^2$
Z. Zheng$^{1,3}$
Q. Lu$^3$
W. Wu$^1$
W. Liu$^1$
Y. Yang$^1$
T. Li$^1$

1 Department of Applied Physics, Harbin Institute of Technology, Harbin 150001, P.R. China
2 Department of Material Physics and Chemistry, Harbin Institute of Technology, Harbin 150001, P.R. China

ABSTRACT The results of the spectroscopic analysis of transition strengths for Er$^{3+}$ ions in a series of Hf:Er:LiNbO$_3$ crystals with variable Hf content and fixed Er content are reported. Unpolarized UV-VIS-NIR absorption spectra, upconversion fluorescence spectra excited at 800 nm, and microsecond time-resolved spectra excited at 400 nm and 800 nm by 800 nm femtosecond laser were measured at room temperature. The HfO$_2$ incorporation has influence on Er$^{3+}$ radiative lifetimes, and fluorescence branching ratios. For Hf(4 mol %):Er(1 mol %):LiNbO$_3$, $\Omega_2 = 2.63 \times 10^{-20}$ cm$^2$, $\Omega_4 = 2.86 \times 10^{-20}$ cm$^2$, and $\Omega_6 = 0.72 \times 10^{-20}$ cm$^2$. $\Omega_2 < \Omega_4$ is contrary to the Er$^{3+}$ general trend of $\Omega_2 > \Omega_4 > \Omega_6$ when the Hf content is below its threshold concentration. In addition, the sum of $\Omega$ increases with the Hf content when the HfO$_2$ content below 6 mol% is unfamiliar. The upconversion mechanism is discussed in this work.

PACS 71.20.Eh; 77.84.Dy; 42.62.Fi; 42.65.Ky

1 Introduction

As an optical material with a large number of interesting properties, LiNbO$_3$ is a widely used. Its excellent electro-optical and acousto-optical coefficients make it is a very good candidate for optoelectronic devices. In addition, the fabrication of LiNbO$_3$ planar waveguides has opened the door to the implementation of this material in integrated optics [1–3]. One of the most promising possibilities is doping with active ions which can be laser in the visible and infrared region [4]. By combining this fact with the nonlinear character of the LiNbO$_3$ matrix, functions such as self-frequency doubling, self-Q-switching and self-mode locking can be achieved. Thus, a big effort is being made to investigate optically active ions in LiNbO$_3$, especial in a family of Ti:Er:LiNbO$_3$ waveguide lasers (amplifiers) and integrated devices [5,6].

Bulk-doped crystals are not the optical solution for guided-wave optics, but they can furnish reliable information for the characterization of locally doped materials.

Pure LiNbO$_3$ as well as Er:LiNbO$_3$ crystals present a low threshold for optical damage [7]. When LiNbO$_3$ devices are used at high laser intensity, their performance is severely limited by optical damage effects, which induces birefringence change and deforms the laser beams [8]. Some photo-damage-resistant dopants have been discovered, including divalent (Mg$^{2+}$ [9], Zn$^{2+}$ [10]), trivalent (In$^{3+}$ [11], and Sc$^{3+}$ [12]), and quadrivalent (Hf$^{4+}$ [13]), which lead to a strong decrease in the optical damage to LiNbO$_3$. For this reason, a lot of research has been undertaken into LiNbO$_3$ crystals doped with photo-damage-resistant dopant. Hf-codoped LiNbO$_3$ crystals have been investigated extensively very recently [14–16], and the light-induced birefringence changes observed in HfO$_2$ 4 mol%: LiNbO$_3$ crystals are comparable to those observed in MgO 6.0 mol%: LiNbO$_3$ ones [17]. In terms of practical application, the spectroscopic properties of Hf:Er:LiNbO$_3$ are needed for further study due to the influence of photo-damage-resistant dopants on the optical properties [18].

In this paper, the unpolarized UV-VIS-NIR absorption spectra of Er:LiNbO$_3$ and Hf:Er:LiNbO$_3$ crystals were measured and the spectroscopic properties were studied based on modified JO theory. The potential transition at 1.5 $\mu$m, 3 $\mu$m, and 550 nm are discussed based on obtained lifetimes and fluorescence branching ratios. The fluorescence spectra and their intensity temporal evolutions were measured in the visible region. The upconverted luminescence mechanism at 800 nm femtosecond laser excitation is also discussed in this work.

2 Experiments

The details of the crystal growth detail can be found elsewhere [39]. Briefly, congruent LiNbO$_3$ crystals were grown along the ferroelectric $c$ axis in air by Czochralski method. The crystals were codoped with Hf$^{4+}$ and Er$^{3+}$ ions in the bulk to a concentration of $X$ ($X = 2, 4, 6, 8$ mol%) and 1 mol% in the crystal-growth melts, respectively. A single doped crystal with Er$^{3+}$ ions to a concentration of 1 mol%
was grown for comparison purposes. The grown crystals were transparent, crack-free, and pink in colour. The boules were polarized by a current density of 5 mA/cm² for 30 min after being maintained at 1200 °C for 6 h in another furnace where the temperature gradient was below 5 K/cm. The samples for testing were cut from the middle of the crystal to rectangular-shaped y-oriented plates, which were then polished to optical grade. Henceforth, these five samples are denoted as Hf-2, Hf-4, Hf-6, Hf-8, and Hf-0, respectively.

Optical absorption spectra were recorded with unpolarized light, with a sample oriented in such a manner that the light propagated along the y axis of the crystal, and with nothing in the reference arm using a Perkin–Elmer Lambda 900 spectrophotometer. The scanning wavelength range was 300–1650 nm. The scanning step and scanning speed were fixed at 1 nm and 300 nm/min, respectively.

Both fluorescence and microsecond time-resolved spectra were carried out in σ-polarization excitation under the Y(XZ)X excitation–probe configuration by using a 120 fs femtosecond laser (Spectra-Physics Spitfire) at 800 nm with a full width at half maximum of 10 nm. The fluorescence propagating along the x axis of the crystal was collected at right angles with respect to the direction of the excitation source by an optical fiber attached to a 25 cm spectrometer (Bruker Chromex 250ts/sm). This included a grating of 150 grooves/mm blazed at 500 nm with a spectral resolution of 0.4 nm, and detected by a thermoelectrically cooled intensified CCD (ICCD, ANDOR). The 400 nm light is the second harmonic generation of 800 nm laser. The laser performed at 1000 Hz and an external trigger from a synchronization delay generator was used to trigger the ICCD in the time-resolved spectra measurements. A position of 1 mm from an edge was excited and side fluorescence was collected from the same edge to minimize the reabsorption of emission. All the measurements were performed at room temperature.

3 Judd–Ofelt theory

Judd-Ofelt theory has been substantially depicted in literature [23]. Some important formulas are briefly presented here. The theoretical transition strength from level i to f can be expressed as the following:

$$f(i, f) = \frac{8\pi^2mc}{3h(2J_i+1)\lambda} \left( \frac{X_{\text{ed}}S_{\text{ed}}}{\epsilon^2} + \frac{X_{\text{md}}S_{\text{md}}}{\epsilon^2} \right)$$  \hspace{1cm} (1)

$$S_{\text{ed}}(i, f) = \epsilon^2 \sum_{\lambda=2,4,6} \Omega_{\lambda} \left| \langle i \parallel U^{(\lambda)} \parallel f \rangle \right|^2$$  \hspace{1cm} (2)

$$S_{\text{md}}(i, f) = \left( \frac{eh}{4\pi mc} \right)^2 \left| \langle S_i L_i J_i \parallel L + 2S \parallel S_f L_f J_f \rangle \right|^2$$  \hspace{1cm} (3)

where $S_{\text{ed}}$ and $S_{\text{md}}$ are electric- and magnetic-dipole oscillator strengths, $\lambda$ is barycenter wavelength at a given absorption band, $m$, $c$ and $h$ are the mass of the electron, light speed in vacuum, and Planck’s constant, respectively. The $L + 2S$ is the magnetic dipole operator, which is independent of host material and can be calculated through formula [24] based on quantum number. The terms $(i \parallel U^{(\lambda)} \parallel f)$ are doubly reduced matrix elements of the unit tensor operator $U^{(\lambda)}$, independent of the host materials, and the values tabulated in [25] are adopted in our calculation. $X_{\text{ed}}$ and $X_{\text{md}}$ are the local field electric dipole and magnetic dipole correction factors, respectively. In the case where one carries out an unpolarized optical absorption measurement on an X- or a Y- cut LiNbO₃ crystal, the $X_{\text{ed}}$ and $X_{\text{md}}$ are given by [26]:

$$X_{\text{ed(md)}} = \frac{X_{\text{ed(md)}}(n_e) + X_{\text{ed(md)}}(n_o)}{2},$$  \hspace{1cm} (4)

where

$$X_{\text{ed}}(n_e,o) = \frac{[n^2_e,o(\lambda) + 2]^2}{9n_e,o(\lambda)}$$  \hspace{1cm} (5)

the terms $n_o$ and $n_e$ are ordinary and extraordinary refractive indices, which are Li-composition dependent and calculated according to the Sellmeier equation [27].

The experimental transition strength can be obtained from the integrated absorption coefficient for each absorption band according to (6):

$$f(i, f)_{\text{meas}} = \frac{4m^2c^2}{N\epsilon^2d(\lambda)} \int \ln(10)OD(\lambda) d\lambda,$$  \hspace{1cm} (6)

where $N$ is the number of rare-earth ions per unit volume, $OD(\lambda)$ is the measurement optical density, and $d$ is the thickness of the crystal. The theoretical transition strength, given by (1), can be fitted to the one from experiment, given by (6), using least-squares fitting, allowing the extraction of the phenomenological JO intensity parameters $\Omega_2, (\lambda = 2, 4, 6)$.

The root mean-square deviation (rms) of the fit $\delta_{\text{rms}}$ is determined by:

$$\delta_{\text{rms}} = \left( \frac{\sum_{i=1}^{I} (f(i, f)_{\text{meas}} - f(i, f)_{\text{calc}})^2}{\text{No. transition} - 3} \right)^{1/2},$$  \hspace{1cm} (7)

where the summation is performed over the total number of absorption bands observed.

Using the obtained intensity parameters, the Einstein A coefficient and excited state radiative lifetime $\tau$ can be calculated by:

$$A_{ij} = \frac{16\pi^3h^2}{3h\epsilon_0(2J_i + 1)(\lambda)^3} \left( X_{\text{ed}}S_{\text{ed}} + X_{\text{md}}S_{\text{md}} \right)$$  \hspace{1cm} (8)

$$\tau_i = \frac{\sum_j A_{ij}}{\sum_j A_{ij}},$$  \hspace{1cm} (9)

where the summation is carried out over all lower-lying level $f$ compared with level $i$.

The fluorescence branching ratio $\beta$ and radiative quantum efficiency $\eta$ is given by:

$$\beta(i, f) = \frac{\tau_i A_{ij}}{\tau_{\text{rad}}}$$  \hspace{1cm} (10)

$$\eta = \frac{\tau_{\text{meas}}}{\tau_{\text{rad}}},$$  \hspace{1cm} (11)

where $\tau_{\text{meas}}$ is measured fluorescence lifetime, and $\tau_{\text{rad}}$ is the calculated one.