Optical properties of LiNbO₃ crystals doped with Yb³⁺ ions

Propiedades ópticas de los cristales de LiNbO₃ dopados con iones Yb³⁺

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ABSTRACT:

Optical properties of Yb-doped LiNbO₃ crystals were investigated. The low temperature absorption and selective emission of LiNbO₃:Yb³⁺ crystals obtained by Montoya et al were reexamined. The LiNbO₃:Yb³⁺ crystals absorption and emission spectra show broad emission due to the presence of four non-equivalent sites: three octahedral sites (Li⁺ (S1), Nb⁵⁺(S2), and a vacant octahedron(S3)) and an interstitial tetrahedral site(S4). Considering the presence of these four Yb³⁺ion-occupied sites, and also the electron-phonon coupling processes, the majority of emission and absorption lines was assigned. For the different observed optical centers in LiNbO₃, the experimental Stark energy levels of Yb³⁺ ions were established.

Keywords: Calcium fluoride, laser ceramic, crystal-field theory, Yb³⁺ions

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1. Introduction

Because of its unique magnetic, non-linear electric, and acousto-optical properties, lithium niobate (LiNbO₃) has been extensively explored in recent decades [1, 2]. LiNbO₃ is a useful material for optical modulators, Pockels cells, optoelectronic tweezers, optical waveguides and optical parametric oscillators due to its great performance [3-6]. As a result, special attention has been paid to the fabrication of LiNbO₃ powders with various morphologies and particle sizes using various techniques, such as sol-gel, combustion methods, hydrothermal, wet chemical methods, molten salt methods [7-11] and surfactant-assisted solution-phase methods [12]. However, due to its nonlinearity [13], the Lithium niobate (LN) crystal is a widely used optical material in laser, photorefractive, and electro-optical applications [14-16]. Using three main techniques, LN crystals were provided with compositions ranging from congruence to stoichiometry, including vapour transport equilibration treatment, crystal growth from the melt and the double crucible method [17-19]. Due to the fact that their $4f^n$ electron states are only mildly influenced by their surroundings, rare-earth ion doped material hosts offer an unsurpassed opportunity to investigate a variety of decoherence mechanisms. Since the $4f^n$ electrons are not involved in chemical bonding, their configuration can display quantum properties similar to those of isolated atoms. Consequently, the study of these systems results not only in materials with optically accessible low decoherence quantum states, but

also in knowledge that can be used in other quantum systems, including RE ions trapped in different LiNbO_3 optical centers. Yb^{3+} has been extensively studied among rare-earth ions due to its simple $4f^{13}$ electronic structure with only two multiplets, which are an excited multiplet $^2F_{5/2}$ and a ground multiplet $^2F_{7/2}$. There has been a resurgence of interest in developing Yb^{3+} doped inorganic materials in recent years. Several potentialities of Yb^{3+} ion in optical materials have been raised for various applications, such as CW and pulsed lasers [20], silicon based solar cells [21-24], upconversion phosphors [25, 26], and biological applications [27, 28]. Yb^{3+} can also be used for structure probe [29, 30], especially for detecting pairing and clustering of doped ions. The intense and broad absorption and emission bands as well as the long lifetime of Yb^{3+} emission are well suited for infrared laser. Thus, various Yb^{3+} ions doped material hosts have been elaborated and tested as tunable lasers and diode-pumped femtosecond [31]. Especially, the niobate families have attracted much interest in providing hosts as laser media for Yb^{3+} laser operation, for instance, $\text{LiNbO}_3:\text{MgO}:\text{Yb}^{3+}$ and $\text{CaNb}_2\text{O}_6:\text{Yb}^{3+}$ phosphor [13, 32].

The presence of dopant ions has a strong influence on the physical behavior of this material. Optical methods have been used to demonstrate the formation of non-equivalent optical sites for a wide range of dopant rare earth (RE) ions. However, the local structure and the site location of these centers are still unknown. It has been reported that the optical spectra of the LiNbO_3 doped by Yb^{3+} ions are particularly sensitive to changes in its surrounding environment. In fact, the existence of four optical Yb^{3+} centers, which was recently published using Temperature dependence of the electron paramagnetic resonance (EPR) lines [33], complicates the interpretation of their optical behaviors and crystal field analysis.

The purpose of this paper is to attempt to reanalyse the optical behavior of $\text{LiNbO}_3:\text{Yb}^{3+}$ taking into account the presence of more than two optical centers and the presence of electron-phonon vibronic effect. The experimental energy levels of the optical centers occupied by Yb^{3+} incorporated in LiNbO_3 have been experimentally determined by using the low temperature emission and polarized absorption spectra reported by Montoya *et al* [34].

2. Experimental details

The low temperature absorption and selectively excited emission spectra of Yb^{3+} ions in LiNbO_3 crystals reported by Montoya *et al* will form the basis for our experimental analysis (figure 1) [34].

Fig.1:(a) Background corrected polarized absorption spectra of $\text{LiNbO}_3:\text{Yb}^{3+}$ at 15K, (b) Background corrected selectively excited emission spectra (excitation wavelength: 915 nm) [34].

As shown in figure 1, the absorption and emission spectra reveal several groups of broadening peaks due to Yb^{3+} ion intra- $4f^{13}$ shell transitions. According to Montoya *et al* [34], several Yb^{3+} centers with slightly different energy levels are contributing to the observed optical behaviors of $\text{LiNbO}_3:\text{Yb}^{3+}$. The determination of the experimental Yb^{3+} ion energy levels occupying these different optical centers has been until now a real problem for all researchers who interested to study the optical behavior of Yb^{3+} ions in LiNbO_3 .

3. Luminescent centers of $\text{LiNbO}_3:\text{Yb}^{3+}$

The trigonal symmetry of the optically transparent host crystal LiNbO_3 [35] is described by the space group C_{3v} , with the optical axis growth parallel to the crystal's c-axis. When compared to ideal stoichiometry, congruent elaboration of $\text{LiNbO}_3:\text{Yb}^{3+}$ samples results in a significant Li^+ deficiency [36], resulting in intrinsic compositional disorder in the LiNbO_3 crystal lattice. Nb^{5+} vacancies, $\text{Li}^+-\text{Nb}^{5+}$ antisites, and oxygen vacancies were also discovered [37, 38].

To understand the optical site occupied by the RE (Yb) ions, it is necessary to establish the optical centers where these Yb^{3+} active ions are doped. As stated above, there are four non-equivalent available centers for Yb^{3+} ions in the LiNbO_3 samples: three octahedral sites (Li^+ (S1), Nb^{5+} (S2) and one empty octahedron (S3)) and one interstitial site tetrahedron (S4) [36-38]. Because of the low Yb^{3+} active ions concentration, X-ray diffraction cannot be used directly to determine their position on the lattice, so other direct or indirect experimental techniques must be used. Since RE ions are heavier than Nb^{5+} , the heavy ion of this host crystal, Rutherford channeling / backscatter spectrometry (RBS) is particularly useful in determining the lattice position of these ions in LiNbO_3 [39-41]. All trivalent RE ions reportedly occupy Li^+ octahedral sites. It has also been shown that RBS can be used to identify embedded Yb^{3+} ions that are off-center from the regular position of Li ions towards the octahedral site space along the c axis [39, 40].

The luminescent center energy levels, which appear in $\text{LiNbO}_3:\text{Yb}^{3+}$ have never been identified because of the complexity behavior of absorption and emission spectra obtained for these samples. In addition to the four optical center contributions, the presence of various phenomena such as vibronic transitions, multiphonon relaxation and (phonon-assisted) energy-transfer processes explains the observed broadening lines [42].

4. Absorption and selective emission spectra investigation of Yb-doped LiNbO_3 crystal

At low temperatures (LT), selective emission and absorption spectra were collected to determine the spectral behaviors of Yb^{3+} ions in a LiNbO_3 host. The free Yb^{3+} ion electronic configuration is $4f^{13}$, with a $^2F_{7/2}$ fundamental energy level and a $^2F_{5/2}$ excited energy level.

The Yb^{3+} activated LiNbO_3 center nature is best revealed by absorption measurements. Figure 1 depicts the LT absorption spectra of $\text{LiNbO}_3:\text{Yb}^{3+}$ in the 900-1020 nm ($9800-11000\text{ cm}^{-1}$) spectral range.

It must be noted that the absorption spectrum of $\text{LiNbO}_3:\text{Yb}^{3+}$ crystals shown in Figure 1 was obtained by subtracting background method with baseline due to the overlap of the Yb^{3+} ion emission band with the vibration modes of the LiNbO_3 crystal. It consists of a series of inhomogeneously broadened bands, each of

which is associated with a transition from the $^2F_{7/2}$ fundamental level to the $^2F_{5/2}$ excited stark energy levels of Yb^{3+} occupying one of the four optical centers in the LiNbO_3 host. The presence of a zero line corresponding to each optical center, which was clearly visible in absorption spectra in the 10140-10240 cm^{-1} spectral range. The presence of these four optical centers occupied by Yb^{3+} in LiNbO_3 is demonstrated in Figure 2(a).

The $^2F_{7/2}(\text{Z0}) - ^2F_{5/2}(\text{E0})$ energy lines corresponding to each center are located at 10186 cm^{-1} (a vacant octahedron), 10192 cm^{-1} (Nb^{5+} site), 10198 cm^{-1} (Li^+ site), 10202 cm^{-1} (interstitial tetrahedral site). In order to determine all of the excited energy levels of Yb^{3+} ions for each optical center we need to investigate the absorption spectra obtained for $\text{LiNbO}_3:\text{Yb}^{3+}$ (fig. 2).

Fig.2: Background corrected absorption spectrum of $\text{LiNbO}_3:\text{Yb}^{3+}$ crystals at low temperature, red line is the Yb^{3+} ion spectral features deconvoluted using partial Gaussian functions. Dot line curves indicate deconvoluted individual Gaussian functions with peak positions indicated by short vertical lines and associated numbers from Table 1

Table 1 summarizes the experimental absorption line values and their attributions. Using these spectra, we determined the experimental Stark energy level positions of the $^2F_{5/2}$ state for each center (Table 2).

Table 1. Absorption spectra line attributed to the different sites of Yb^{3+} in $LiNbO_3$ crystal shown in Fig.2.

Line	E_{obs} (cm $^{-1}$)	Attribution ^{a, b}
1	10186	$F_0 \rightarrow F_4$ (S3)
2	10192	$F_0 \rightarrow F_4$ (S2)
3	10198	$F_0 \rightarrow F_4$ (S1), $F_3 \rightarrow F_6$ (S4)
4	10202	$F_0 \rightarrow F_4$ (S4), $F_3 \rightarrow F_6$ (S3)
5	10377	$F_3 \rightarrow F_6 + E_{TO2}$ (S1), $F_2 \rightarrow F_5 + E_{TO3}$ (S3)
6	10421	$F_3 \rightarrow F_5 + E_{TO7}$ (S2), $F_0 \rightarrow F_4 + E_{TO2}$ (S3)
7	10446	$F_1 \rightarrow F_6$ (S4)
8	10466	$F_1 \rightarrow F_4 + A1_{TO4}$ (S1), $F_3 \rightarrow F_6 + E_{TO6}$ (S2), $F_0 \rightarrow F_4 + E_{TO3}$ (S4)
9	10483	$F_0 \rightarrow F_5$ (S3)
10	10504	$F_0 \rightarrow F_5$ (S4)
11	10561	$F_1 \rightarrow F_5 + E_{TO1}$ (S2)
12	10576	$F_0 \rightarrow F_5$ (S2)
13	10604	$F_3 \rightarrow F_5 + A1_{TO4}$ (S4)
14	10624	$F_0 \rightarrow F_5$ (S1)
15	10646	$F_1 \rightarrow F_6 + E_{TO2}$ (S2)
16	10683	$F_0 \rightarrow F_6$ (S2)
17	10700	$F_0 \rightarrow F_6$ (S3)
18	10729	$F_0 \rightarrow F_6$ (S4)
19	10744	$F_0 \rightarrow F_6$ (S1)
20	10777	$F_0 \rightarrow F_5 + E_{TO1}$ (S1), $F_0 \rightarrow F_4 + E_{TO8}$ (S1)
21	10830	$F_0 \rightarrow F_4 + A1_{TO4}$ (S1), $F_0 \rightarrow F_5 + A1_{TO1}$ (S2)
22	10840	$F_0 \rightarrow F_5 + E_{TO3}$ (S2)
23	10852	$F_0 \rightarrow F_6 + E_{TO1}$ (S3)
24	10862	$F_0 \rightarrow F_5 + E_{TO2}$ (S1)
25	10878	$F_0 \rightarrow F_5 + A1_{TO1}$ (S1)
26	10888	$F_0 \rightarrow F_5 + E_{TO3}$ (S1)
27	10897	$F_0 \rightarrow F_6 + E_{TO1}$ (S1)
28	10916	$F_0 \rightarrow F_5 + E_{TO7}$ (S3)
29	10937	$F_0 \rightarrow F_5 + E_{TO7}$ (S4), $F_0 \rightarrow F_6 + E_{TO2}$ (S3)

^a S₁, S₂, S₃ and S₄ used in the attribution designed the four optical centers occupied by Yb^{3+} in $LiNbO_3$.

^b the A₁ and E phonon mode values are listed in table 3.

Table 2. Experimental crystal field energy levels (in cm^{-1}) of Yb^{3+} ions occupied different optical centers in LiNbO_3 crystals.

Optical centers	Multiplet	S. levels ^a	Exp.val ^b
Yb_{Li^+}	$^2\text{F}_{5/2}$	F_6	10744
		F_5	10624
		F_4	10198
	$^2\text{F}_{7/2}$	F_3	605
		F_2	504
		F_1	364
		F_0	0
$\text{Yb}_{\text{Nb}^{5+}}$	$^2\text{F}_{5/2}$	F_6	10683
		F_5	10576
		F_4	10192
	$^2\text{F}_{7/2}$	F_3	588
		F_2	440
		F_1	275
		F_0	0
$\text{Yb}_{\text{S}3}$	$^2\text{F}_{5/2}$	F_6	10699
		F_5	10483
		F_4	10186
	$^2\text{F}_{7/2}$	F_3	488
		F_2	370
		F_1	246
		F_0	0
$\text{Yb}_{\text{S}4}$	$^2\text{F}_{5/2}$	F_6	10729
		F_5	10504
		F_4	10202
	$^2\text{F}_{7/2}$	F_3	532
		F_2	329
		F_1	283
		F_0	0

^a Stark level splitting of the manifold levels $^{2S+1}L_J$.

^b Experimental energy levels (in cm^{-1}) observed in the absorption and emission spectra in this study for different optical centers occupied by Yb^{3+} ions.

It should be mentioned that the presence of a hot band in the absorption spectra of $\text{LiNbO}_3:\text{Yb}^{3+}$ (figure 2(d)) is not attributed to the inter $4f^n$ transition of Yb^{3+} ions which make the interpretation of this band difficult and not evident. The presence of this anomalous band located at 10878 cm^{-1} , and the broadening in this observed band proves the presence of electron-phonon coupling phenomena. In fact, lattice phonons are of the order of the Stark splitting of rare earth (RE) ions. The electron-phonon coupling produces modified (nonadiabatic) vibronic states when the distance between two Stark electronic levels is close to resonance with phonon peaks observed in LiNbO_3 Raman spectra. As a result, the optical spectral line shapes change (broadening, asymmetries, or splitting). Such effects have been observed in organic and inorganic [43] compounds, particularly for RE ions at the start and end of the lanthanide series. Because Yb^{3+} has a strong vibronic coupling, resonant effects could be observed in LiNbO_3 [44]. Table 3[45] lists the $\text{E}(\text{TO})$ and $\text{A1}(\text{TO})$ phonon values reported for LiNbO_3 crystals.

Table 3. Experimental Raman scattering (in cm^{-1}) reported for LiNbO_3 [45].

Mode	Raman scattering (cm^{-1})
E(TO1)	153
E(TO2)	238
E(TO3)	264
E(TO4)	323
E(TO5)	361
E(TO6)	371
E(TO7)	433
E(TO8)	579
E(TO9)	665
A1(TO1)	254
A1(TO2)	278
A1(TO3)	333
A1(TO4)	632

All the peaks observed in this broad band were attributed to the presence of these resonant effects. In the aim to establish the excited stark energy levels of Yb^{3+} occupied different optical centers, we investigate the selective emission spectra ($\lambda_{\text{exc}} = 915 \text{ nm}$) performed at low temperature (LT) for $\text{LiNbO}_3:\text{Yb}^{3+}$ in the 960-1100 nm spectral range.(figure 1). The deconvoluted selective emission spectrum of $\text{LiNbO}_3:\text{Yb}^{3+}$ is shown in Fig. 3.

Fig.3: Background corrected selective emission spectra of $\text{LiNbO}_3:\text{Yb}^{3+}$ crystals at low temperature, red and green lines are the Yb^{3+} ion spectral features deconvoluted using partial Gaussian functions. Dot line curves indicate deconvoluted individual Gaussian functions with peak positions indicated by short vertical lines and associated numbers from Table 4.

It is clearly seen that all emission spectra reveal a group of broadening peaks corresponding to Yb^{3+} intra-4f n shell transition originated from different $^2\text{F}_{5/2}$ excited Stark levels (F4, F5, F6) to the $^2\text{F}_{7/2}$ ground state (F0, F1, F2, F3) of Yb^{3+} ion in LiNbO_3 host corresponding to the four non-equivalent optical centers (S1, S2, S3 and S4). In addition, we note the presence of add peaks explained by electron-phonon coupling phenomena. All the observed peaks and their attribution are collected in the table 4.

Table 4. Emission spectra line attributed to the different sites of Yb^{3+} in LiNbO_3 crystal shown in Fig.3

Line	E_{obs} (cm^{-1})	Attribution ^{a, b}
1	9308	$F_4 \rightarrow F_1$ - A1 _{TO4} (S3)
2	9323	$F_4 \rightarrow F_2$ -E _{TO6} (S1)
3	9337	$F_4 \rightarrow F_3$ -A1 _{TO3} (S4)
4	9350	$F_4 \rightarrow F_3$ - A1 _{TO1} (S2)
5	9361	$F_4 \rightarrow F_2$ -A1 _{TO3} (S1), $F_4 \rightarrow F_1$ - E _{TO8} (S3)
6	9383	$F_4 \rightarrow F_2$ - E _{TO7} (S3), $F_4 \rightarrow F_2$ - E _{TO6} (S2)
7	9393	$F_5 \rightarrow F_3$ - E _{TO8} (S4)
8	9401	$F_4 \rightarrow F_1$ - E _{TO7} S(1)
9	9416	$F_4 \rightarrow F_2$ -A1 _{TO2} (S1), $F_5 \rightarrow F_3$ - E _{TO8} (S3), $F_4 \rightarrow F_3$ - A1 _{TO1} (S4),
10	9432	$F_4 \rightarrow F_3$ -E _{TO2} (S4)
11	9445	$F_4 \rightarrow F_2$ - E _{TO6} (S3)
12	9463	$F_6 \rightarrow F_3$ -A1 _{TO4} (S2), $F_4 \rightarrow F_1$ - E _{TO6} (S1),
13	9503	$F_4 \rightarrow F_2$ - E _{TO6} (S4), $F_4 \rightarrow F_1$ - A1 _{TO3} (S1),
14	9593	$F_4 \rightarrow F_3$ (S1)
15	9604	$F_4 \rightarrow F_3$ (S2)
16	9617	$F_5 \rightarrow F_3$ - E _{TO6} (S2), $F_4 \rightarrow F_1$ -E _{TO4} (S3),
17	9660	$F_6 \rightarrow F_2$ - E _{TO8} S(1), $F_6 \rightarrow F_2$ - E _{TO8} (S2),
18	9670	$F_4 \rightarrow F_3$ (S4)
19	9708	$F_5 \rightarrow F_3$ -E _{TO3} (S4)
20	9724	$F_6 \rightarrow F_3$ - E _{TO6} (S2), $F_5 \rightarrow F_3$ - E _{TO3} (S2)
21	9752	$F_4 \rightarrow F_2$ (S2)
22	9895	$F_6 \rightarrow F_2$ - E _{TO7} (S3)
23	9907	$F_6 \rightarrow F_2$ - A1 _{TO3} (S1)
24	9920	$F_4 \rightarrow F_1$ (S4)
25	9948	$F_4 \rightarrow F_0$ - A1 _{TO1} (S4), $F_4 \rightarrow F_0$ - E _{TO2} (S3),
26	9962	$F_6 \rightarrow F_2$ - A1 _{TO2} S(1)
27	9995	$F_5 \rightarrow F_3$ (S3)
28	10091	$F_6 \rightarrow F_2$ - E _{TO1} (S2), $F_6 \rightarrow F_2$ - E _{TO2} (S2),
29	10175	$F_5 \rightarrow F_2$ (S4)

^a S₁, S₂, S₃ and S₄ used in the attribution designed the four optical centers occupied by Yb^{3+} in LiNbO_3 .

^b the A₁ and E phonon mode values are listed in table 3.

The assignment of all observed lines in absorption and emission spectra has been established which confirm the consistence of the obtained experimental energy levels of Yb^{3+} ions occupied the different optical centers. Comparing the observed and the emission spectra obtained for Yb^{3+} in LiNbO_3 , we note that the electron-phonon coupling cause a blue shift of Yb^{3+} intra-4f n shell transition in the absorption spectra whereas for the emission spectra we have found that this interaction causes a red shift.

5. Conclusions

The optical investigation has been done at low temperature for $\text{LiNbO}_3:\text{Yb}^{3+}$ crystals. The feature of $\text{LiNbO}_3:\text{Yb}^{3+}$ crystals shows the presence of four optical centers, corresponding to three octahedral optical centers (Li^+ , Nb^{5+} , and a vacant octahedron) and an interstitial tetrahedral site. Using the selective emission and the absorption spectra of Yb^{3+} in LiNbO_3 crystals, the experimental Stark energy states of Yb^{3+} ions incorporated in LiNbO_3 crystals were established for all of obtained sites. The presence of electron-phonon interaction have been confirmed in these samples. The assignment of all observed lines in absorption and emission spectra has been established which confirm the consistence of the obtained experimental energy levels of Yb^{3+} ions occupied the different optical centers. The observed broadening in the line shapes were investigated.