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SPECTRA, ENERGY LEVELS AND UP-CONVERSION EFFECT OF ERBIUM IONS IN $LiNbO_3$ CRYSTALS*

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The Optical properties and spectral data of erbium-doped Lithium Niobate crystals, including absorption spectrum, emission spectrum, luminescence lifetime and up-conversion effects are reported in this paper. The energy level scheme, Stark splitting under crystal field and up-conversion mechanism are discussed in detail. The possible applications of this material in waveguide optics and opto-electronics are also prospected.

PACC: 4270; 7170E; 7855

I. INTRODUCTION

The spectral properties and energy level attribution of Er^{3+} ions in crystals of CaF_2, $LiYF_4$, $YAlO_3$ and YAG etc. were investigated earlier[1], but those in $LiNbO_3$ crystals, to our knowledge, have not been reported till now. Recently, more attention has been paid to the waveguide laser action of $Er:LiNbO_3$ crystal, especially in the wavelength range near 1.5 μm, which is currently used in fiber communications. It is further attempted to integrate waveguide laser or amplifier, waveguide modulators and switches on a single $LiNbO_3$ substrate. In the respect of experiment, Brinkmann *et al.*[2] reported for the first time a waveguide laser of Er^{3+} in $LiNbO_3$ crystal substrate, employing ion implantation of Er^{3+} and diffusion of Ti to fabricate waveguide. They obtained 1.53 μm waveguide laser output on the order of micro-watts; the output was rather low, but it still arouses much interest because of its apparent novelty and applicability. In order to test the realisable possibility of applying $Er:LiNbO_3$ crystal in fabricating waveguide laser or amplifier, and provide experimental results as basic data for device design if necessary, we report in this paper the spectra, energy levels and other spectral data in some detail. The frequency up-conversion effect of $Er:LiNbO_3$ was also observed and described in this paper, which may be useful in the compact visible solid state laser pumped by laser diode (infrared).

II. EXPERIMENTAL

Large size and optical grade $Er:LiNbO_3$ crystal, as well as $Er:Mg:LiNbO_3$ crystal, was for the first time grown in our laboratory (Chinese Patent ZL 91100010.0). The former was used in the spectral measurement. The concentration of dopant Er^{3+} in $Er:LiNbO_3$ is 0.4, 1.2 and 2.0 at% and labeled as #1, #2 and #3, respectively. The crystals are machined to x-cut or z-cut wafers of 1 mm thick, ground and polished for spectral measurement.

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Absorption spectrum of $Er:LiNbO_3$ was measured at 300 K in the range of 0.18-2.5 μm with a spectrophotometer of type UV-3600, Shimadzu. Fluorescent emission spectra of samples at 300 K were measured with a Spex-FIII AI fluorescence spectrometer. Fluorescence spectrum with higher resolution at 10 K was measured by L. McCaughen and his coworkers in Wisconsin-Madison University, USA. Fluorescence spectrum in the range near 1.5 μm was measured by W. Sohler and his coworkers in University of Paderborn, Germany. The samples they measured were provided by our laboratory with the same dopant concentration. Measurement of fluorescent lifetime was performed with a Laser Flash Photolysis in Central Laboratory of Photochemistry, Academia Sinica. The exciting light source of the photolysis is a pulsed laser with wavelength 532 nm and pulse width 6–7 ns, fluorescent measurement is in the range of 250–950 nm with a time resolution of 50 ps.

III. RESULTS AND DISCUSSIONS

A. Spectroscopic data and Stark energy splitting

The absorption spectrum of $Er:LiNbO_3$ (sample #2) at room temperature is shown in Fig. 1. This spectrum appears in sharp line-like structure, indicating that the spectrum character of rare earth ion in the crystal is different from that of Er-doped glass (fiber)[3], in which only some peak envelopes (wide band structure) can be observed. In comparison with the spectra of Er^{3+} ions in other crystal hosts, such as YAG[4], there are similarities in spectrum structure but different in peak positions and peak intensities, indicating different effect of different crystal field.

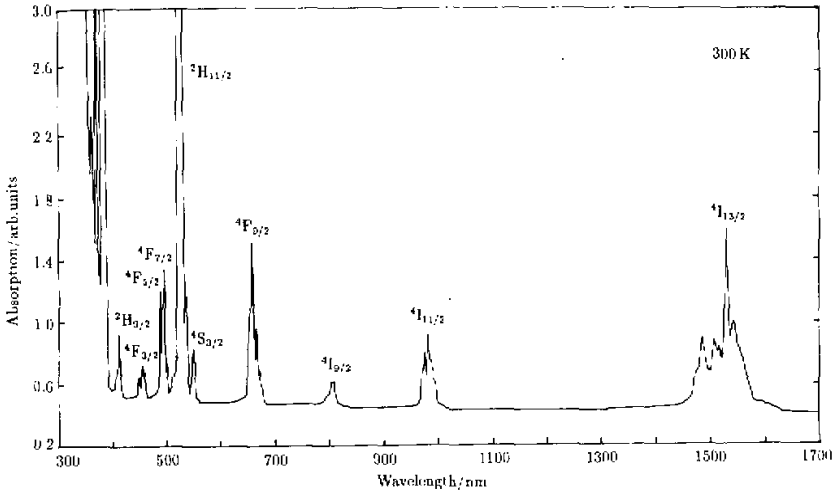

Fig. 1. Absorption spectrum of $Er:LiNbO_3$.

According to Fig. 1 and Figs. 4, 5 (to be shown later), we determined the spectral terms

and energy levels of Er : $LiNbO_3$ crystal, as shown in Fig. 2. In this level scheme we considered only spin-orbit coupling of an Er^{3+} ion, but did not take account of Stark splitting yet.

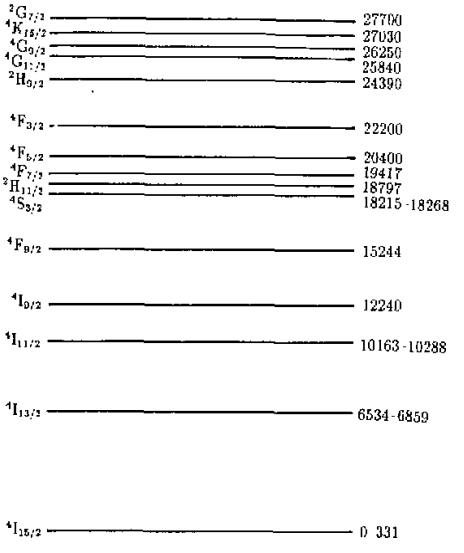

Fig. 2. Energy levels of Er : $LiNbO_3$ (a cm^{-1} is a unit of energy level).

In order to determine Stark splitting of each term, more precise spectral data are necessary. The fluorescence spectrum of sample #2 excited by the light of 515 nm is shown in Fig. 3. There are two strong emission peaks corresponding to the transitions from two branches of state $^4S_{3/2}$ to ground state $^4I_{15/2}$. At their short wave edge and long wave edge there are two sets of emission peaks with wavelengths around 532 and 670 nm, respectively, corresponding to the transitions from states $^2H_{11/2}$ and $^4F_{9/2}$ to ground state. A high resolution spectrum of the same sample corresponding to the first transition measured at 10 K is shown in Fig. 4, which shows the fine structure of Stark splitting. In Fig. 4 there are many spectral lines showing doublet structure, in which the difference of the two lines is only 0.1–0.2 nm in wavelength.

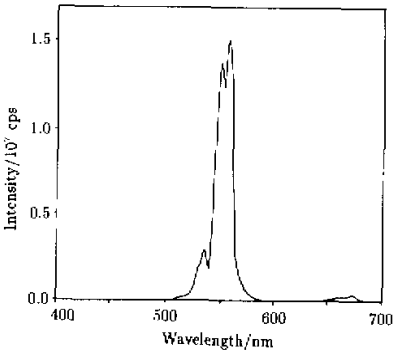

Fig. 3. Emission spectrum of Er : $LiNbO_3$ at 300 K, λ_{ex} = 515 nm.

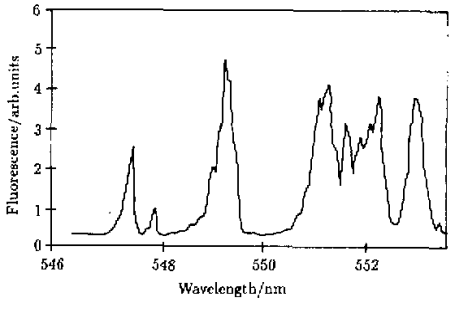

Fig. 4. Emission spectrum of Er : $LiNbO_3$ at 10 K, λ_{ex} = 453.4 nm.

In $LiNbO_3$ crystal lattice, Er^{3+} ions are seated at the centers of distorted oxygen octahedra. The symmetry of the crystal field is not high, so only Kramer degeneration exists in the spectral term. As the number of Stark splitting components belonging to $^{2S+1}L_J$ is $(2J + 1)/2$, the Stark splitting level number of the state $^4S_{3/2}$ is 2 and that of $^4I_{15/2}$ is 8.

From the data of spectra corresponding to the transition $^4S_{3/2} \longrightarrow {}^4I_{15/2}$ given in Figs. 3 and 4, we can determine the Stark splitting of the two states. Satisfactory results can be easily obtained since the state $^4S_{3/2}$ has only two Stark components.

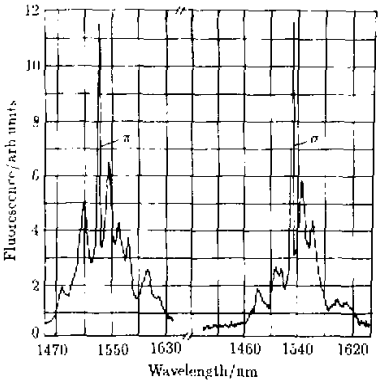

Fig. 5. Fluorescence spectrum of transition $^4I_{13/2} \longrightarrow {}^4I_{15/2}$ at 300 K, $\lambda_{ex} = 657.7$ nm.

The fluorescent spectrum corresponding to the transitions from $^4I_{13/2}$ to $^4I_{15/2}$ is shown in Fig. 5, where excitation light is tuned to 657 nm and π polarization. It can be seen from the figure that the position and height of the 1.53 μm central peak in π and σ components are similar, but their side bands are different.

From the spectroscopic data of the transition from $^4I_{13/2}$ to $^4I_{15/2}$ given in Fig. 5, we can determine the Stark level of state $^4I_{13/2}$, when the Stark level of $^4I_{15/2}$ has been determined. Some data of Stark level we considered are summarized in Table 1.

For any peak position of fluorescence emission spectra shown in Figs. 3, 4 and 5, a corresponding transition between levels in Table 1 can be found. The "doublet structure" of some spectral lines is perhaps contributed by the perturbation of Stark levels due to the small difference of crystal fields, since there are two different sites in $LiNbO_3$ crystal lattice, i.e., Li site and Nb site, which can be replaced by Er^{3+} ion. This kind of effect of rare earth ion in other crystals has been reported[5], but a report of that in $LiNbO_3$ has not been seen.

Table 1. Some Stark splitting levels.

Term	Stark splitting level/cm^{-1}
$^4I_{15/2}$	0, 17, 60, 126, 136, 159, 195, 331
$^4I_{13/2}$	6534, 6592, 6609, 6770, 6807, 6849, 6859
$^4S_{3/2}$	18215, 18268

We are interested in the transitions between levels of $^4I_{13/2} \longrightarrow {}^4I_{15/2}$ and $^4S_{3/2} \longrightarrow {}^4I_{15/2}$, because the former is related to the generation of 1.5 μm waveguide laser and the latter is related to up-conversion of infrared to green light output.

B. Fluorescent lifetime

The decay curve of fluorescence corresponding to transition $^4S_{3/2} \longrightarrow {}^4I_{15/2}$ measured by a Laser Flash Photolysis is shown in Fig. 6, where the pump light used is of 532 nm wavelength and 6–7 ns pulse width, and the channel width is 0.4 μs/channel.

According to $I = I_0 \exp(-t/\tau_{lum})$, we have lifetime

$$\tau_{lum} = \frac{0.4343t}{\log I_0 - \log I}.$$

From Fig. 6 we obtain $\tau_{lum} = 35\ \mu$s directly.

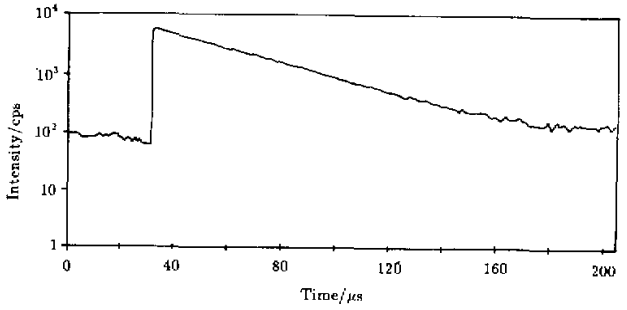

Fig. 6. Decay curve of fluorescence of 557 nm in Er : $LiNbO_3$ at 300 K, $\lambda_{ex} = 530$ nm.

We could not measure the lifetime of fluorescence with wavelength 1.53 μm due to limitation of equipment, but we used a comparatively simple method to estimate it. In the case of pure radiative transition and Lorentz line shape, the Füchtbauer-Ladenburg formula

$$\sigma_e = \frac{\lambda^4 A_{21}}{4\pi^2 n^2 c \Delta\lambda},$$

and

$$A_{21} = \frac{1}{\tau_{lum}}, \quad \sigma_e = \sigma_a = \frac{\alpha}{N_1}$$

can be used. If the absorption coefficient α has been given, the effective cross-section of stimulated emission and absorption, σ_e and σ_a, can be estimated and then the spontaneous emission coefficient A_{21} and luminescence lifetime τ_{lum} can be calculated. In the formula, n is the refractive index of the crystal, N_1 is the particle number concentration at ground state. For the distribution coefficient of Er^{3+} in the crystal $LiNbO_3$ is nearly equal to 1, we can estimate N_1 from the dopant concentration.

From a series of calibrated absorption spectra with central peak at wavelength 1.53 μm of different samples #1, #2 and #3, absorption coefficients α and spectral widths $\Delta\lambda$ were measured for different beam arrangements. Table 2 gives related spectral parameters for various Er^{3+} doping concentrations and light beam arrangements.

Table 2. Emission cross-section and lifetime in Er : $LiNbO_3$ ($\lambda = 1.53\,\mu$m).

	Direction: x, Polarization: π			Direction: x Polarization: σ			Direction: z		
Sample	#1	#2	#3	#1	#2	#3	#1	#2	#3
$\sigma_e/10^{-20}\,cm^2$	1.28	1.20	1.13	1.94	1.85	1.68	3.07	2.96	2.57
τ_{lum}/ms	16.0	15.5	13.9	13.2	11.8	11.1	9.3	8.7	8.0

From the data given in Table 2, some conclusions can be drawn: (1) In the case of fluorescence emission of 1.53 μm, the emission cross-section and fluorescence lifetime of Er : $LiNbO_3$, $\sigma_e = 2 \times 10^{-20}\,cm^2$ and $\tau_{lum} = 10$ ms, are relatively higher than those of Er : YAG crystal, $\sigma_e = 5 \times 10^{-21}\,cm^2$ and $\tau_{lum} = 6.4$ ms[4]. (2) Both σ_e and τ_{lum} are related to transmission

and polarization direction of pumping beam. From Table 2 we can see that the largest σ_e is in z-transmission, then in x-transmission π polarization. This fact is perhaps useful in the design of $Er:LiNbO_3$ waveguide laser or amplifier. (3) Er^{3+} dopant concentrations of the samples labeled #1, #2, #3 are 0.4, 1.2, 2.0 at%, respectively. Data in Table 2 shows both σ_e and τ_{lum} decrease as Er^{3+} concentration increases, indicating the concentration quench effect of fluorescence. Since the Er^{3+} concentration is not very high, quenching does not cause serious situation, but the tendency is clear.

From the viewpoint of laser generation of $Er:LiNbO_3$ at wavelength 1.53 μm, the laser running scheme is a three-level system. This is the main drawback of the crystal used in this wavelength. Fortunately, the lifetime of the excited state is sufficiently large, so the difficulty is lessened and the lasing or amplification action can be realized.[2]

C. Effect of up-conversion

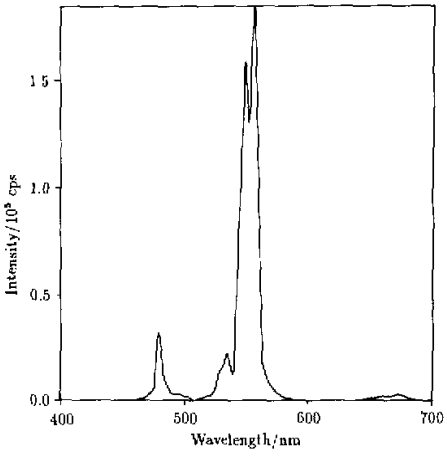

Fig. 7. Emission spectrum of up-conversion in $Er:LiNbO_3$ ($\lambda_{ex} = 960$ nm).

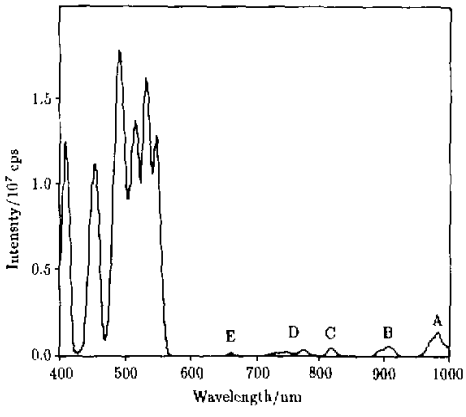

Fig. 8. Emission Spectrum in $Er:LiNbO_3$ (including up-conversion) ($\lambda_{ex} = 557$ nm).

There exist several excited states of long lifetime in $Er:LiNbO_3$, for example, the lifetime of state $^4I_{13/2}$ is 10 ms, as pointed above. The lifetime of state $^4I_{11/2}$ is also on the order of ms, so it is easy to induce excited state absorption (ESA). In addition to other energy transfer mechanism, $Er:LiNbO_3$ crystal has a lot of up-conversion effects. In recent years the investigation of up-conversion has become active[6] and this effect of Er^{3+} ions in other crystals has been reported early[7], but the report of the up-conversion effect in $Er:LiNbO_3$ crystal was few. In fact, $Er:LiNbO_3$ possesses strong up-conversion emission, at least for the green light of wavelength 550–557 nm. Using a small electric torch to illuminate the crystal, one can observe remarkable green fluorescence even with naked eyes. Figure 7 shows the emission spectrum excited by infrared light (960 nm) at 300 K. Compared with Fig. 3 where exciting light is 515 nm, the luminescence peaks are identical, except a peak of 480 nm which may come from other source. The fact that infrared light of 960 nm generates the green light

of 550 nm indicates the up-conversion effect in Er : $LiNbO_3$ crystal definitely.

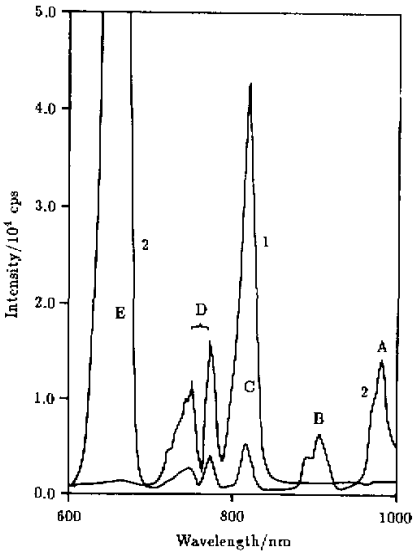

Fig. 9. Excitation spectrum of up-conversion (curve 1: λ_{em} = 410 nm; curve 2: λ_{em} = 670 nm).

The excitation spectrum of the green fluorescence of 557 nm (corresponding to $^4S_{3/2} \longrightarrow {}^4I_{15/2}$) is shown in Fig. 8. With respect to the central wavelength 557 nm, the peaks on the short wave side are normal excitation spectrum (down-conversion), and those on the long wave side are up-conversion one. In Fig. 8 we can see that there are five groups of peaks in the up-conversion excitation spectrum labeled A, B, C, D, E. In general, the intensity of fluorescence by up-conversion excitation is much weaker than that of normal excitation. It is estimated that up-conversion excitation is about one tenth of the normal excitation.

Er : $LiNbO_3$ can also emit blue and red fluorescence through up-conversion excitation. The up-conversion excitation spectra of emission wavelengths 410 and 670 nm are shown in Fig. 9. Comparing Fig. 8 with Fig. 9, we can conclude that the up-conversion excitation peaks are actually identical for the emission of blue, green and red wavelengths.

Table 3. Emission and excitation wavelengths of up-conversion in Er : $LiNbO_3$.

Emission/nm	Excitation of up-conversion/nm				
	A	B	C	D	E
410			822	774, 750	659
550	984, 972	908, 894	817	774, 749	658
670	984, 972	908, 893	818	775, 749	

Table 3 summarizes the exciting wavelengths for the 410, 550 and 670 nm emission in the up-conversion. Here the group A (λ_{ex}=984, 972 nm) corresponds to the transition

$^4I_{15/2} \longrightarrow {}^4I_{11/2}$, the group C ($\lambda_{ex} = 817\,nm$) corresponds to $^4I_{15/2} \longrightarrow {}^4I_{9/2}$ and the group E ($\lambda_{ex} = 659\,nm$) corresponds to $^4I_{15/2} \longrightarrow {}^4F_{9/2}$. Lifetimes of the three excited states are sufficiently long, so that ESA may take place with greater possibility. The processes mentioned above were shown in Fig. 10 schematically.

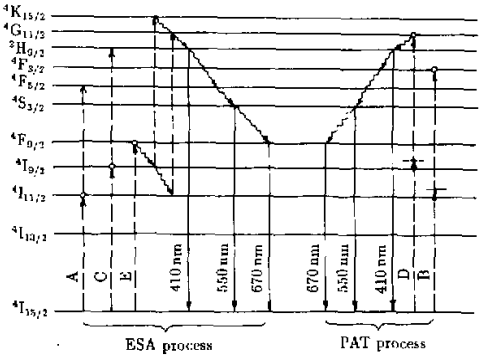

Fig. 10. Schematic diagram of up-conversion for 410, 550, 670 nm emission.

A difficulty arises from the interpretation of the excitation wavelengths 908, 893 nm and 774, 750 nm (the group B and D in Figs. 8, 9 and Table 3), which could not be found in the absorption spectrum shown in Fig. 1. This situation is shown on the right side of Fig. 10 schematically. There could be many mechanisms to explain this fact. For example: (1) Some sort of transition assisted by phonons may exist in the excitation process of the crystal, so there may be a "virtual middle state" between the ground state and the high excited state. (2) $LiNbO_3$ possesses strong optical nonlinearity. There always exists SHG fluorescence under illumination of exciting light. If the fluorescence is exactly the resonance wavelength of high excited state, it acts as a normal exciting light in turn. (3) Perhaps there exists some sort of two-photon absorption process that induces transition from ground state to the high excited level directly. Obviously, it is necessary to investigate and clarify these points through further experimental and theoretical work.

IV. CONCLUSIONS

In this paper, we have reported for the first time the data of Stark splitting energy levels, lifetime and effective cross-section of fluorescence, emission and excitation spectra of the $Er:LiNbO_3$ crystal, noticed and discussed the site selectivity in Stark splitting levels, the anisotropy and concentration quench in lifetime and cross-section of fluorescence, ESA and other possible mechanism in up-conversion excitation.

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