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Up-conversion in Er^{3+}-doped $LiNbO_3$ crystals

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Abstract

Frequency up-conversion luminescence and the excitation spectra of Er^{3+} ions in $LiNbO_3$ crystals have been studied at room temperature. The observed up-conversion luminescence bands have peaks at about 410, 550 and 670 nm, while the excitation bands have peaks at 774, 749 and 658 nm for the 410 nm luminescence, at 984, 908, 893, 817, 774, 749 and 658 nm for the 550 nm luminescence, and at 984, 908, 893, 817, 774 and 749 nm for the 670 nm luminescence. From a comparison of the excitation-band spectra for the luminescence with the absorption spectra, it is suggested that a two-photon absorption process and an excited state absorption process occur in parallel in the up-conversion. Sharp 410 and 480 nm lines were observed under 820 and 960 nm excitation, respectively. These lines are suggested to be the second harmonic radiation from the nonlinear $LiNbO_3$ bulk crystal.

Keywords: Er^{3+}-doped $LiNbO_3$; Excited state absorption; Luminescence; Two-photon absorption; Up-conversion

1. Introduction

Recently, much work has been devoted to up-conversion luminescence in rare-earth-ion-doped materials. The up-conversion is a process where excitation with lower energy radiation gives rise to higher energy luminescence. Many investigators have studied the up-conversion in Er^{3+}-doped crystals and glasses such as Er^{3+}:$LiYF_4$, Er^{3+}:LaF_3 and Er^{3+}:$YAlO_3$ [1–6]. There are a few papers on the up-conversion in Er^{3+}:$LiNbO_3$ crystals [7,8], especially on the green up-conversion luminescence. No study has been undertaken on other up-conversion luminescence, although Er^{3+} gives rise to various luminescence bands in many bulk materials [1–6] and Er^{3+}:$LiNbO_3$ is important as a waveguide and electro- and acoustooptical devices [9].

The trivalent rare-earth ions in $LiNbO_3$ occupy the Li^+ octahedron but they are slightly shifted from the Li^+ regular position [10]. In Er^{3+}:$LiNbO_3$, energy transfer between two adjacent Er^{3+} ions at Li^+ sites has been observed to possibly give rise to up-converted green luminescence when they are in the excited states, in addition to up-conversion due to the excited state absorption process [11].

Nunez et al. [7] obtained the excitation spectrum for each of the 560.1 nm green luminescence in Er^{3+}:$LiNbO_3$ and found that the up-converted luminescence is produced by the excitation not at a special wavelength but over a limited spectral region. From comparison of the excitation band shape with the Er^{3+} absorption spectrum, they suggested that the $^4I_{15/2}\rightarrow{}^4I_{9/2}$ transition occurs in the first step of the sequential two-step absorption for the up-conversion. It is interesting to investigate (1) whether the other Er^{3+} absorption bands can possibly produce the green up-converted luminescence in $LiNbO_3$, (2) what kind of other up-converted luminescence is possible, and (3) what kinds of processes (e.g. multi-photon absorption, excited state absorption, energy transfer) give rise to the up-conversion.

2. Experimental procedure and results

Large single crystals of Er^{3+}-doped $LiNbO_3$ were grown using the Czochralski method at Tianjin University. Special care (e.g., re-crystallization) was taken to distribute the Er^{3+} ions in the crystals uniformly and to grow large crystals. The largest size obtained was 100 mm long with a diameter of 40 mm. Three kinds of crystals with 0.2, 0.6 and 1.0 mol% Er^{3+} concentrations were grown. The crystals were *X*- and *Z*-cut and polished. The thickness used for the optical measurements was 1 mm. Absorption spectra were recorded with a Shimadzu UV-3100 spectrophotometer. The luminescence and excitation spectra were recorded using a Spex F111 AI fluorescence spectrometer, equipped with a 500 W Xe lamp.

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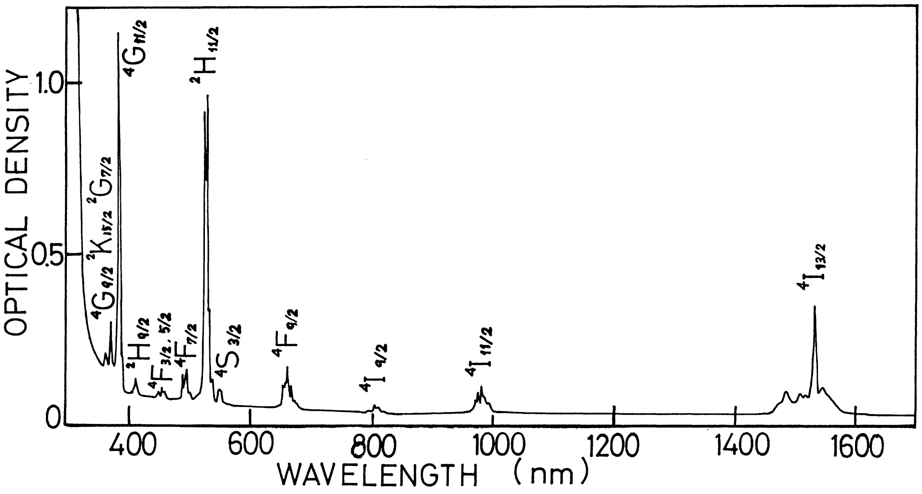

Fig. 1. Absorption spectrum of Er^{3+} ions (0.2 mol%) in a $LiNbO_3$ crystal at 296 K. The excited states are indicated on the absorption bands.

The absorption spectrum of a *Z*-cut Er^{3+}:$LiNbO_3$ crystal at 296 K is shown in Fig. 1. It is quite similar to the spectra of other Er^{3+}-doped crystals. Several absorption bands with sharp lines are observed in the 350–1600 nm region, which are due to the $f^{11} \rightarrow f^{11}$ electronic transitions, i.e. transitions from the $^4I_{15/2}$ ground state of Er^{3+} to the excited states. The excited states of these bands are indicated in Fig. 1.

Several luminescence bands are produced by the excitation in the Er^{3+} absorption bands. Their luminescence bands have peaks at about 1530, 670, 550 and 410 nm. Fig. 2 shows the up-conversion luminescence spectrum observed under excitation with 960 nm light at 296 K. Four luminescence bands are observed at about 670, 550, 530 and 480 nm. These bands, except for the 480 nm band, have a doublet structure. The same luminescence spectrum (but without the 480 nm band) was observed by the excitation with 515 and 454 nm light, which corresponds to the excitation of the higher $^2H_{11/2}$ and $^4F_{5/2}$ states, respectively.

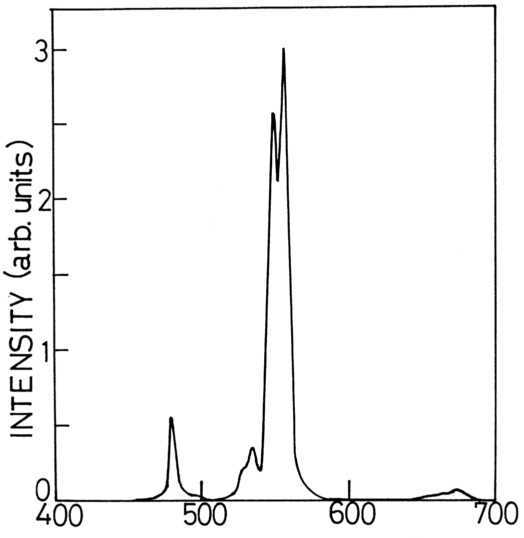

Fig. 2. Up-conversion luminescence spectrum of Er^{3+}:$LiNbO_3$ by excitation with 960 nm light at 296 K.

The excitation spectrum for the 550 nm up-conversion luminescence was observed to consist of seven bands with peaks at about 984, 908, 893, 817, 774, 749 and 658 nm, which are respectively called bands A, B, C, D, E, F and G hereafter. The same excitation spectrum was obtained for the 670 nm luminescence, as shown by the solid line in Fig. 3a. The F band has a triplet structure, the components of which are named F_1, F_2 and F_3 in order of increasing energy. In the case of the 410 nm up-conversion lumines-

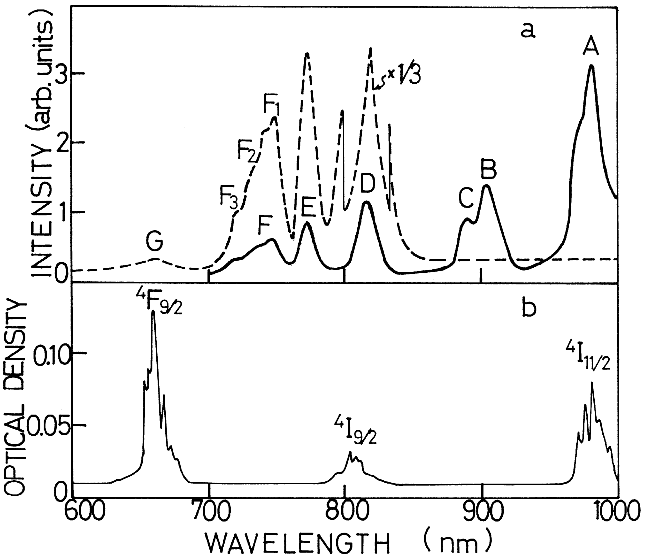

Fig. 3. Excitation spectra for the up-converted 670 nm (———) and 410 nm (- - -) luminescence at 296 K (a), compared with the absorption spectrum at 296 K (b). The spectrometer resolution used in the excitation spectrum measurement was adjusted to be much wider, about 15 nm, than the resolution (0.2 nm) used in the absorption measurement, because of the weak up-conversion luminescence intensity.

cence, the excitation bands are only the E, F and G bands together with a sharp intense 820 nm peak, as shown by the broken line in Fig. 3a. Thus, the A, B, C and D bands, which are observed in the excitation spectrum for the 670 nm luminescence, were not observed, i.e. no excitation band appears at a wavelength longer than 840 nm.

The 550 nm luminescence was also observed to have excitation bands peaking at about 490, 455 and 410 nm. This is a Stokes luminescence where lower energy luminescence is produced by the excitation with higher energy radiation. These three excitation bands correspond to the absorption bands due to the $^4I_{15/2}\rightarrow{}^4F_{7/2}$, $^4F_{5/2}+{}^4F_{3/2}$ and $^2H_{9/2}$ transitions, respectively. The intensities of these excitation bands are higher by a factor of more than 10 than those of the A–G excitation bands for the anti-Stokes (i.e. up-conversion) 550 nm luminescence.

When the excitation spectrum for the 670 nm up-conversion luminescence is compared with the absorption spectrum, the A and G excitation bands are coincident with the absorption bands due to the $^4I_{15/2}\rightarrow{}^4I_{11/2}$ and $^4F_{9/2}$ transitions, respectively, as shown in Fig. 3, if the resolution of the band structure is neglected, while the D band is coincident with the low energy component of the absorption band due to the $^4I_{15/2}\rightarrow{}^4I_{9/2}$ transition.

3. Discussion

The up-conversion luminescence bands appearing at 515–580 and 660–680 nm in Fig. 2 are coincident with those obtained by excitation of the $^4S_{3/2}$ and $^4F_{9/2}$ levels. Therefore, taking into account the luminescence band positions, these bands are attributable to the transitions $^4S_{3/2}\rightarrow{}^4I_{15/2}$ and $^4F_{9/2}\rightarrow{}^4I_{15/2}$, respectively [12]. Regarding the 410 nm luminescence, it is attributable to the $^2H_{9/2}\rightarrow{}^4I_{15/2}$ transition from the energy of the $^2H_{9/2}$ level. This is consistent with the identification of Auzel [13], who observed the 410 nm luminescence in Er^{3+}:YF_3 crystals.

Of the A–F excitation bands which give rise to the 550 nm $^4S_{3/2}\rightarrow{}^4I_{15/2}$ luminescence (see Fig. 3a), the A, D and G bands are coincident with the transitions from the $^4I_{15/2}$ ground state to the $^4I_{11/2}$, $^4I_{9/2}$ and $^4F_{9/2}$ states, respectively. Therefore, in this up-conversion via D and G band excitation it is suggested that electrons are excited from the $^4I_{15/2}$ ground state to the $^4I_{9/2}$ and $^4F_{9/2}$ states in the first step, relax to the lower $^4I_{11/2}$ state nonradiatively, and then rise from the $^4I_{11/2}$ state to higher states $^4F_{7/2}$ and $^2H_{9/2}$, respectively, by excited state absorption due to light of the same energy used in the first step, as shown in Fig. 4. Finally, the excited electrons relax to the lower-energy $^4S_{3/2}$ state nonradiatively, and then give rise to the 550 nm luminescence. Here, we choose the $^4I_{11/2}$ state as the relaxed state from the $^4I_{9/2}$ and $^4F_{9/2}$ states, because the lifetimes of the $^4F_{9/2}$ and $^4I_{9/2}$ states are known to be much shorter than that of the $^4I_{11/2}$ state in many host lattices such as $LiYF_4$, $CaYAlO_4$, $GaAlO_3$ and $YAlO_3$ [13–17] and so the excited state absorption from these states should also be weaker in Er^{3+}:$LiNbO_3$.

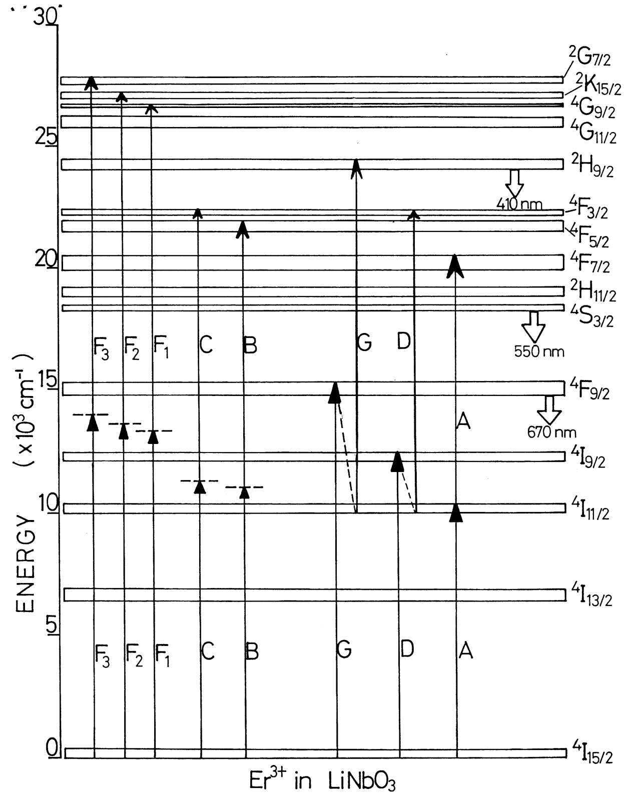

Fig. 4. Energy level diagram for Er^{3+} in a $LiNbO_3$ crystal and up-conversion 410, 550 and 670 nm luminescence by the two-photon absorption process (left) and by the excited state absorption process (right). The broken horizontal line indicates the virtual level in the two-photon absorption. The energy levels are drawn taking into account the absorption bandwidth at room temperature.

When the electrons are excited to the $^4I_{11/2}$ state directly by A band excitation, it is suggested that the electrons are raised to the $^4F_{7/2}$ state by excited state absorption from the $^4I_{11/2}$ state (see Fig. 4). Similarly, the 670 nm up-conversion luminescence produced by A and D band excitation and the 410 nm luminescence by G band excitation are suggested to occur through the excited state absorption process. The transition process shown in Fig. 4 is consistent with the fact that the 410 nm luminescence is not produced by D band excitation.

On the other hand, the B, C, E and F excitation bands observed for the 550 nm (and also 670 nm) luminescence, as well as the E and F bands for the 410 nm luminescence, are not coincident with any Er^{3+} ground-state absorption band. In this case the electrons are not excited to the Er^{3+} excited states directly by a single photon. It is suggested that electrons are excited to a virtual level by the first photon and then excited from the virtual level to the higher Er^{3+} state by the second photon with the same energy as the first photon, i.e. electrons are excited to a higher state by absorbing simultaneously two photons with the same energy: this process is called two-photon absorption.

To examine the possibility of the two-photon absorption process, we plotted the two-photon excitation spectrum for the 670 nm luminescence (Fig. 5, broken line), i.e. the luminescence intensity was plotted versus the doubled photon energy of the radiation used to obtain the excitation spectrum of Fig. 3a. The one-photon ground-state absorption spectrum (which is the same as Fig. 1) is also shown in Fig. 5 (see solid line). When the two-photon excitation spectrum, which consists of the B, C, E and F (composed of F_1, F_2 and F_3) two-photon-excitation bands (called B′, C′, E′ and F′ (F_1', F_2' and F_3') bands, respectively), is compared with the ground-state absorption spectrum, it is observed that the F_1', F_2' and F_3' bands are located at the same photon-energy position as the absorption bands due to the $^4I_{15/2}\rightarrow{}^4G_{9/2}$, $^2K_{15/2}$ and $^2G_{7/2}$ transitions, respectively. Similarly, it is observed that the B′ and C′ bands are located at the same position as the $^4I_{15/2}\rightarrow{}^4F_{5/2}$ and $^4F_{3/2}$ absorption bands, respectively. The whole lineshape of the B′ and C′ bands is quite similar to that of the two absorption bands if the spectral resolution is neglected. On the other hand, the E′ band is located at almost the same position as the lowest-energy component of the $^4I_{15/2}\rightarrow{}^4G_{11/2}$ absorption band. From these results, it is suggested that the 550 nm or 670 nm up-conversion luminescence via the B, C and F_1, F_2 and F_3 excitation bands is caused by excitation from the ground state to the $^4F_{5/2}$, $^4F_{3/2}$, $^4G_{9/2}$, $^4K_{15/2}$ and $^2G_{7/2}$ states, respectively, by two-photon absorption, as shown on the left side of Fig. 4.

The 480 nm band is observed in the emission spectrum for the 960 nm excitation wavelength in Fig. 2. Unlike the other excitation bands, the 480 nm band has a single (i.e. non-structure) and sharp peak with narrow bandwidth. Therefore, taking into account that (1) 480 nm is just half of 960 nm, (2) $LiNbO_3$ is a nonlinear crystal which has been used as a second harmonic generator, and (3) there is no ground-state absorption at 960 nm, the 480 nm luminescence is attributed not to the Er^{3+} luminescence but to the second harmonic radiation of the exciting 960 nm light. The same is true for the sharp peak at 820 nm which was observed in the excitation spectrum for the 410 nm luminescence: the 410 nm radiation is produced as the second harmonic of the 820 nm radiation. Our result is consistent with the recent observation of second harmonic generation in Er^{3+}:$LiNbO_3$ by a 1064 nm Nd^{3+}:YAG laser pump at room temperature [8]. The 410 nm radiation was observed to be more intense than the 410 nm up-conversion luminescence. This is also consistent with Ju et al.'s observation [8] that the second harmonic intensity is much higher than the up-conversion luminescence.

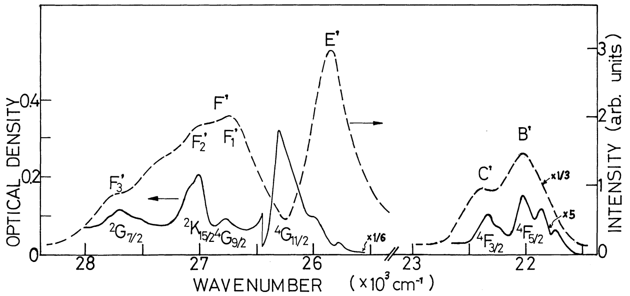

Fig. 5. Two-photon excitation spectrum (- - -, scale on the right) for the 670 nm up-conversion, compared with the one-photon absorption spectrum (———, scale on the left).

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