

## Enhancement of $\text{Er}^{3+}$ Luminescence in $\text{LiNbO}_3:\text{Mg}$ Crystals \*

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The luminescent properties of  $\text{Er}^{3+}$  ions in  $\text{LiNbO}_3:\text{Er}$  and  $\text{LiNbO}_3:\text{Mg,Er}$  crystals at room temperature have been investigated by the emission spectra and the selective excitation spectra. The energy transition processes of  $\text{Er}^{3+}$  luminescence have been analysed. It has been found that the luminescent intensity of  $\text{Er}^{3+}$  ions in the  $\text{LiNbO}_3:\text{Mg,Er}$  crystal increased up to 7.8 times compared with that in the  $\text{LiNbO}_3:\text{Er}$  crystal. The decrease of the defect centre ( $\text{Nb}_{\text{Li}}$ ) concentration due to doping with  $\text{Mg}^{2+}$  ions plays a key role in this phenomenon.

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The lithium niobate ( $\text{LiNbO}_3$ ) crystal is a promising candidate for opto-electronic devices, such as optical waveguides,<sup>[1]</sup> photorefractive devices<sup>[2]</sup> and some laser elements<sup>[3]</sup> due to its electro-optical and nonlinear optical properties. However, up to now, its luminescent intensity has not been strong so that many researchers have been exploring new ways to obtain a high bright luminescence in the  $\text{LiNbO}_3$  crystal.

Since Johnson and Ballman<sup>[4]</sup> reported coherent stimulated emission in rare-earth ions doped in  $\text{LiNbO}_3$  crystals, many efforts have been taken to investigate optically rare-earth ions in the crystals. Among these, few studies have been devoted to co-doped lithium niobate crystals.<sup>[5,6]</sup>

The luminescence of rare-earth ions depends strongly on the crystalline environment, which is mainly determined by the occupation of active ions. Co-doping with  $\text{Mg}^{2+}$  ions will change its intrinsic defect structure greatly in the  $\text{LiNbO}_3$  crystal doped with rare-earth ions, and then will affect the luminescence of the rare-earth ions. In this letter, the luminescent mechanism of  $\text{Er}^{3+}$  ions in  $\text{LiNbO}_3:\text{Er}$  and  $\text{LiNbO}_3:\text{Er,Mg}$  crystals at room temperature are investigated. Our results definitely illustrate that co-doping of the alkaline earth metal ions and the rare-earth ions into the  $\text{LiNbO}_3$  crystals is an effective way to obtain the high bright luminescence of the rare-earth ions.

The  $\text{LiNbO}_3$  crystals used in our experiment were grown by the Czochralski method. One of the samples was doped by 0.2 mol% Er and the other was co-doped by 0.2 mol% Er and 4.0 mol% Mg. The crystals were cut and polished with their faces parallel or perpendicular to the ferroelectric  $c$ -axis. The emission spectra and selective excitation spectra were measured by a SPEX Fluorolog-2 spectrometer at room temperature, and were not obviously different for the various

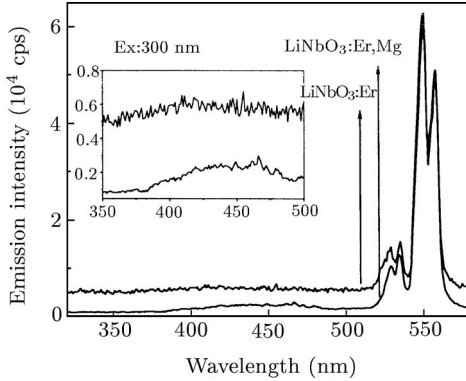
orientations of the samples.

The absorption edge of the  $\text{LiNbO}_3$  crystal was near 320 nm at room temperature. Therefore, the emission spectra of  $\text{LiNbO}_3:\text{Er}$  and  $\text{LiNbO}_3:\text{Er,Mg}$  crystals were measured first by Xe lamp excitation at 300 nm wavelength, as shown in Fig. 1. Here, we give the emission spectrum in the visible range. The emission peaks are located at 529, 535, 550 and 558 nm, respectively. These emissions peaks correspond to the transitions from  ${}^4F_{5/2}$ ,  ${}^4F_{7/2}$ ,  ${}^2H_{11/2}$  and  ${}^4S_{3/2}$  to  ${}^4I_{15/2}$ , respectively. A weak broad emission band within the range of 400–480 nm is found in the  $\text{LiNbO}_3:\text{Er,Mg}$  crystal, which results from the intrinsic defect emission of the crystal. However, the intrinsic defect emission is not observed in the  $\text{LiNbO}_3:\text{Er}$  crystal. Fischer *et al.*<sup>[7]</sup> found that the emission intensity of the intrinsic defect in the  $\text{LiNbO}_3:\text{Mg}$  crystal enhances to two orders of magnitude compared to that of the undoped crystal at 80 K. In  $\text{LiNbO}_3:\text{Er,Mg}$  crystals,  $\text{Mg}^{2+}$  ions replace  $\text{Nb}_{\text{Li}}$  and consequently the  $\text{Nb}_{\text{Li}}$  concentration is diminished.  $\text{Nb}_{\text{Li}}$  is a quenching centre of radiation, so the weak broad emission band is observed in  $\text{LiNbO}_3:\text{Er,Mg}$  crystals.

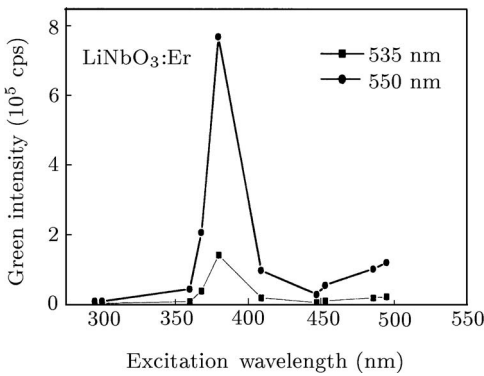
The emission intensity ratio  $I_{529}/I_{535}$  in the  $\text{LiNbO}_3:\text{Er}$  crystal is nearly the same as that in  $\text{LiNbO}_3:\text{Er,Mg}$  crystals, as is the ratio of  $I_{550}/I_{558}$ . However, the ratios  $I_{529}/I_{550}$ ,  $I_{535}/I_{550}$  and  $I_{529}/I_{558}$  are different in the two crystals, as shown in Fig. 1. This means that the non-emission relaxation probability between Er energy levels in the two samples is different. The different non-emission relaxation probability shows that the two samples have different crystalline environments. In the same crystal, the relative intensity of transitions from  ${}^4F_{5/2}$ ,  ${}^4F_{7/2}$ ,  ${}^2H_{11/2}$  and  ${}^4S_{3/2}$  to  ${}^4I_{15/2}$  does not change, which is shown in Fig. 2, when the excitation wavelength is less than

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500 nm, i.e. the excitation light energy is larger than the emission light energy. However, the relative intensities of every emission peak are different in the different crystals.



**Fig. 1.** Emission spectra of LiNbO<sub>3</sub>:Er and LiNbO<sub>3</sub>:Er, Mg crystals. (ex. 300 nm).

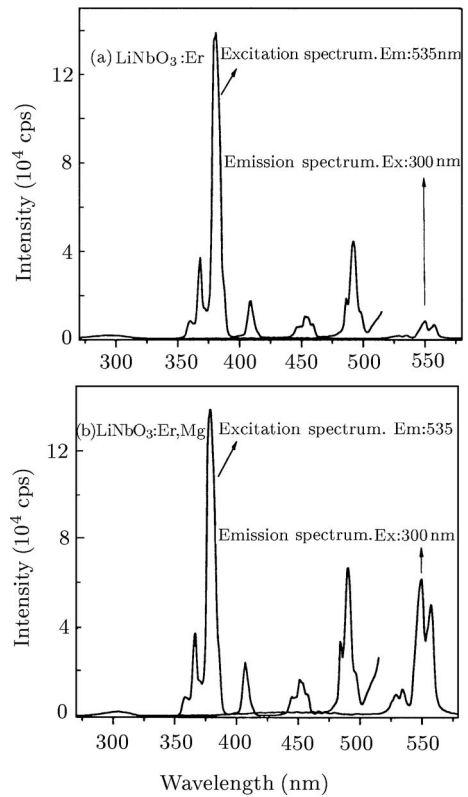


**Fig. 2.** Dependence of the relative intensity peaks at 535 nm (550 nm) on the excitation wavelength.

The different crystalline environments of Er<sup>3+</sup> ions in LiNbO<sub>3</sub>:Er and LiNbO<sub>3</sub>:Er,Mg crystals result in different photoluminescent intensities. To analyse the energy transfer mechanism of Er<sup>3+</sup> ions in LiNbO<sub>3</sub>:Er and LiNbO<sub>3</sub>:Er,Mg crystals, the selective excitation spectra were measured, as shown in Fig. 3. The relative intensity of every absorption peak in the same crystal is not changed when the 529, 535, 550 and 558 nm emissions are monitored. This shows that the relative intensity of Er<sup>3+</sup> emission at 529, 535, 550 and 558 nm will be the same in the same crystal by using excitation light with a wavelength less than 500 nm. However, the relative intensity of every absorption peak in different crystals is different. The absorption peaks at 359, 368, 380, 408, 445, 451 and 491 nm correspond to the transitions from <sup>4</sup>I<sub>15/2</sub> to <sup>4</sup>G<sub>7/2</sub>, <sup>4</sup>G<sub>9/2</sub>, <sup>4</sup>G<sub>11/2</sub>, <sup>2</sup>H<sub>9/2</sub>, <sup>4</sup>F<sub>3/2</sub>, <sup>4</sup>F<sub>5/2</sub> and <sup>4</sup>F<sub>7/2</sub>. The absorption intensity ratio of I<sub>359</sub>/I<sub>368</sub>/I<sub>380</sub>/I<sub>408</sub>/I<sub>445</sub>/I<sub>451</sub>/I<sub>491</sub> is 0.06:0.27:1.00:0.13:0.04:0.08:0.32 and 0.060:0.27:1.00:0.18:0.07:0.12:0.49 in LiNbO<sub>3</sub>:Er and LiNbO<sub>3</sub>:Er,Mg crystals, respectively. The variation of the relative

absorption intensity in the two crystals implies the crystalline environment change of Er<sup>3+</sup> ions.

The weak broad absorption band in the vicinity of 300 nm of selective excitation spectra, which is shown in Fig. 3, is the intrinsic absorption of the LiNbO<sub>3</sub> crystal.<sup>[8]</sup> Its peak locates at 291 nm in LiNbO<sub>3</sub>:Er crystals and at 304 nm in LiNbO<sub>3</sub>:Er,Mg crystals, which shows that the intrinsic absorption edge shifts to the long wavelength in LiNbO<sub>3</sub>:Er,Mg crystals. The full width at half maximum (FWHM) of the intrinsic absorption band is the same (30 nm) as that in the two crystals.



**Fig. 3.** Selective excitation spectra in LiNbO<sub>3</sub>:Er and LiNbO<sub>3</sub>:Er,Mg crystals (Em. 535 nm): (a) LiNbO<sub>3</sub>:Er crystal; (b) LiNbO<sub>3</sub>:Er,Mg crystal.

In the experiments, we found that the luminescent intensity of Er<sup>3+</sup> ions is enhanced obviously in the LiNbO<sub>3</sub>:Er,Mg crystal. In order to compare the luminescent intensity of Er<sup>3+</sup> ions in the same conditions, the emission spectra in the two crystals are measured by using Xe lamp excitation ( $\lambda = 300$  nm) while the intensity of the strongest absorption peak (at 380 nm) is kept the same. The results are shown in Fig. 3. The emission intensity of Er<sup>3+</sup> ions in the LiNbO<sub>3</sub>:Er,Mg crystal is about 7.8 times that in the LiNbO<sub>3</sub>:Er crystal, which definitely shows that the luminescence of Er<sup>3+</sup> ions in the LiNbO<sub>3</sub>:Er,Mg crystal could be enhanced greatly by co-doping Mg<sup>2+</sup> ions into the crystals.

As we know from the Judd–Ofelt (J–O) theory, the probability for an emission transition from state  $i$  to state  $j$ ,  $A_{ij}$ , is given by:

$$A_{ij} = \frac{64\pi^4\nu^3e^2}{3h(2J+1)c^3} \cdot \frac{n(n^2+2)^2}{9} \cdot (\Omega_2U_2 + \Omega_4U_4 + \Omega_6U_6),$$

where  $\nu$  is the frequency,  $e$  is the electron charge,  $h$  is the Planck constant,  $c$  is the velocity of light, and  $n$  is the refractive index of the host glass.<sup>[10]</sup>  $J$  is the quantum number of angular momentum of the initial state in the transition.  $U_2$ ,  $U_4$  and  $U_6$  are doubly-reduced matrix elements of the tensor operator of a transition from the initial state  $i$  to the final state  $j$ .  $\Omega_2$ ,  $\Omega_4$  and  $\Omega_6$  are the J–O parameters, which show the disorder strength of the crystal in the surroundings of the  $\text{Er}^{3+}$  ions. In the  $\text{LiNbO}_3$  crystal, Mg doping changes the defect structure greatly<sup>[11]</sup> and consequently the environment of  $\text{Er}^{3+}$  ions changes. Therefore, the  $\text{Er}^{3+}$  luminescent intensity will change obviously in the  $\text{LiNbO}_3\text{:Er,Mg}$  crystal.

In the  $\text{LiNbO}_3\text{:Er,Mg}$  crystal, Mg ions replace  $\text{Nb}_{\text{Li}}$ , which changes the defect group  $(\text{Nb}_{\text{Li}})^{4+} - 4(\text{V}_{\text{Li}})^{-}$  to  $(\text{Mg}_{\text{Li}})^{+} - (\text{V}_{\text{Li}})^{-}$  according to the Li-site vacancy model.<sup>[11]</sup> As a result, the  $\text{Nb}_{\text{Li}}$  concentration is decreased after doping with Mg ions. Due to the decrease of the quench centres ( $\text{Nb}_{\text{Li}}$ ), more energy will be transferred to  $\text{Er}^{3+}$  ions and the emission of  $\text{Er}^{3+}$  ions is enhanced in the  $\text{LiNbO}_3\text{:Er,Mg}$  crystal.

In summary, the emission properties of  $\text{Er}^{3+}$  ions in the  $\text{LiNbO}_3\text{:Er}$ , and  $\text{LiNbO}_3\text{:Er,Mg}$  crystals at room temperature are analysed by the emission spec-

tra and selective excitation spectra. The emission intensity of  $\text{Er}^{3+}$  ions in the  $\text{LiNbO}_3\text{:Er,Mg}$  crystal is enhanced by 7.8 times compared with that of  $\text{LiNbO}_3\text{:Er}$  crystals because the co-doping with  $\text{Mg}^{2+}$  ions results in the decrease of the concentration of the quenching centre  $\text{Nb}_{\text{Li}}$ . Our results show that the luminescent change of  $\text{Er}^{3+}$  ions in  $\text{LiNbO}_3\text{:Er,Mg}$  crystals could be used to probe the change of the defect structure in  $\text{LiNbO}_3$  crystals and co-doping with Mg is an effective way to enhance the luminescent intensity of rare-earth ions in the  $\text{LiNbO}_3$  crystals.

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