Influences of Mg^{2+} ion on dopant occupancy and upconversion luminescence of Ho^{3+} ion in $LiNbO_3$ crystal*

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The effects of a Mg^{2+} ion on the dopant occupancy and upconversion luminescence of a Ho^{3+} ion in $LiNbO_3$ crystal are reported. The birefringence gradient of the crystal is measured to investigate the optical homogeneity. The X-ray powder diffraction spectrum and the upconversion luminescence are used to investigate defect structure and spectroscopic properties of Mg,Ho:$LiNbO_3$. Under 808-nm excitation, blue, red, and very intense yellow-green bands are observed. Based on the energy levels of Ho^{3+} in $LiNbO_3$, and the pump intensity dependence of the observed emission, an excitation scheme is presented. The upconversion emission spectra reveal an enhancement of upconversion intensity when the Mg^{2+} ions are introduced into Ho:$LiNbO_3$. The main upconversion mechanism is discussed in this work.

Keywords: Mg,Ho:$LiNbO_3$, upconversion luminescence, optical homogeneity

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1. Introduction

$LiNbO_3$, a technological material with a large number of interesting properties, is widely used. Its excellent piezoelectric, nonlinear-optical, electro-optical, and acousto-optic property make it a very good candidate for optoelectronic devices. The first upconversion phenomenon observed by Bloembergen in 1959 was in crystal doped by a rare-earth (R) ion.[1] In 1973, Auzel[2] was the first one to review and explore it. In recent years, upconversions in rare earth ion doped crystals have been widely studied because of their applications in colour display, optoelectronics, medical diagnostics, and optical data storage. In 2004, Arizmendi[3] reported that R^{3+} doped $LiNbO_3$ is one of the most relevant systems in optoelectronics since it combines the good spectroscopic properties of R^{3+} and the outstanding nonlinear properties of the $LiNbO_3$ host. Upconversion is a nonlinear process, which mainly occurs in a rare earth ion (R^{3+}) doped system. It is based on the presence of more than one electronically excited metastable state in R^{3+}. The R ions serve as potential active ions for laser materials due to their good luminescent properties.[4,5]

In rare earth ions, the trivalent holmium ion (Ho^{3+}) constitutes an intriguing active ion for upconversion emission, due to its convenient energy level structure, which is exploitable in upconversion processes. Thus, many researchers have paid their attention to the upconversion emissions of Ho^{3+} ions. Unfortunately, although the upconversion luminescence properties of Ho^{3+} ions have been extensively studied for a variety of solid state matrices, information about the Ho:$LiNbO_3$ system is scarce. Because R^{3+}-doped $LiNbO_3$ crystal presents a low threshold for photorefractive damage, optical-damage-resistant dopants (Mg^{2+}, Zn^{2+}, Sc^{3+}, In^{3+}, Zr^{4+}, and Hf^{4+}) are usually doped to improve the performance of $LiNbO_3$.[6–12]

In this work, congruent Ho(1 mol%):$LiNbO_3$ crystals codoped with different concentrations of Mg^{2+} ion (1 mol%, 3 mol%, 5 mol%, 7 mol%, and 10 mol%) are grown using the Czochralski technique in optimized growth conditions. XRD and optical homogeneity are used to investigate the effect of Mg^{2+} ion on the dopant occupancy of Ho^{3+} ion in $LiNbO_3$ crystal. The upconversion emission spectra, the power pump dependence, and the upconversion mechanism are investigated to understand the influence of the Mg^{2+} ion on the upconversion luminescence of a Ho^{3+} ion in $LiNbO_3$ crystal.

2. Experiments

2.1. Crystal growth

Mg,Ho:$LiNbO_3$ crystals were grown in air by using the Czochralski method from a congruent melt ([Li]/[Nb] = 0.946).[13] The raw materials for crystal growth were Li_2CO_3, Nb_2O_5, MgO, and Ho_2O_3 with the 4N purities. The doping concentration of Ho_2O_3 was 0.5 mol%, and concentrations of MgO were chosen to be 1 mol%, 3 mol%, 5 mol%, 7 mol%, and 10 mol%, respectively. In order to remove CO_2,

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the mixtures were heated up to 750 °C for 2 h, and then sequentially up to 1050 °C for 2 h. Consequently, the polycrystalline powders were formed as starting materials. The crystals were grown under optimum conditions: temperature gradient of 40 °C/cm–50 °C/cm, rotation rate of 10 rpm–25 rpm (1 rpm = 1 r/min) and pull rate of 0.5 mm/h–2 mm/h. In our experiment, grown crystals were polarized at 1200 °C with a current density of 5 mA/cm^2. Then, the grown crystals were cut into y-cut plates with a size of 10 mm×20 mm×2 mm ($x \times z \times y$) and the two opposite sides of the surface were optically polished. Henceforth, these five samples are denoted by Mg/Ho-1/1, Mg/Ho-3/1, Mg/Ho-5/1, Mg/Ho-7/1, and Mg/Ho-10/1, respectively.

2.2. Optical measurements

A small portion of the grown crystal was crushed properly and the crystal powder was analysed using a SHIMADZU XRD-6000 diffractometer.[14] The measurement conditions were as follows: the wavelength was 0.15419 nm (pure Cu Kα radiation), tube voltage/tube current was 40 kV/50 mA, and machine scanning range was $2\theta = 20°$–$80°$.

The birefringence gradient experiment was conducted to study the optical homogeneity of the crystal. An He–Ne laser of $\lambda = 633$ nm was used as a light source. The sample was placed between a pair of crossed polarizes. Moreover, a quarter wave plate was inserted between the sample and the analyzer. The experimental setup is shown in Fig. 1. The birefringence gradient ΔR is calculated by[15]

$$\Delta R = \frac{\partial(n_o - n_e)}{\partial x} = \frac{\lambda}{\pi d}\frac{\Delta\phi}{\Delta x}, \tag{1}$$

where Δx is the distance between the two measured points, d is the crystal thickness, $\Delta\phi$ is the extinction angle difference between the two measured points, and λ is the wavelength of the laser beam in vacuum.

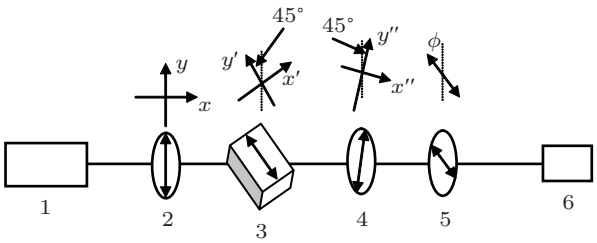


Fig. 1. Experimental setup for birefringence gradient measurement. Numbers 1–6 represent He–Ne Laser, polarizer, sample, $\lambda/4$ wave plate, analyzer, detector, respectively.

Upconversion emission spectra of Mg,Ho:$LiNbO_3$ and microsecond time-resolved spectra were measured under excitation at 808 nm (with the full width at half maximum of 10 nm) using a Ti:sapphire femtosecond laser. Power dependence was measured by using neutral density filters. All experiments were performed at room temperature.

3. Results and discussion

3.1. X-ray powder diffraction spectrum

The XRD experimental results are shown in Fig. 2. The lattice parameters are calculated by using the least-square method. The unit cell values are given by the formula $V = (a^2c)\cos(30°)$. According to the above results, we conclude that the doping of the Mg^{2+} ion and the Ho^{3+} ion did not create a new diffraction peak.[16] This demonstrates that the entry of Mg^{2+} and Ho^{3+} into the lattice of $LiNbO_3$ does not charge the crystal structure greatly. The radii of incorporated Mg^{2+} and Ho^{3+} are different from those of Li^+ and Nb^{5+} in the lattice of $LiNbO_3$, so the unit cell volume, shape, and atomic position are slightly changed and in turn the position of diffraction peak in the diffraction pattern changes. The radii of Mg^{2+}, Ho^{3+}, Li^+, and Nb^{5+} ions are 0.66 Å, 0.9 Å, 0.68 Å, and 0.69 Å respectively,[17] according to the ion radius approximation principle in the crystal field theory, Mg^{2+} and Ho^{3+} ions enter into crystal lattices by replacing Li^+ and Nb^{5+} ions other than by occupying the slot between crystal lattices. The XRD measurement results are shown in Table 1. It can be seen clearly that, in the samples, the lattice constants increase with Mg^{2+} concentration increasing, thus the unit cell volume of crystals also increase. According to the Li-vacancy model,[18] Mg and Ho ions will enter into the lattice by replacing Nb_{Li}^{4+} and form Mg_{Li}^{+} and Ho_{Li}^{2+} defects. At the same time, the concentration of Li-vacancies will increase and electro-neutrality is maintained, which can lead to the expansion of the crystal lattice. Therefore, the lattice constants and the cell volume become larger. When the Mg^{2+} concentrations are 7 mol% and 10 mol% in the melt, i.e., above the threshold values (Mg/Ho-7/1, Mg/Ho-10/1) (at a certain doping level, all Nb_{Li}^{4+} ions are completely replaced by Mg ions, and this doping level of Mg^{2+} in $LiNbO_3$ crystal is called the "threshold concentration".

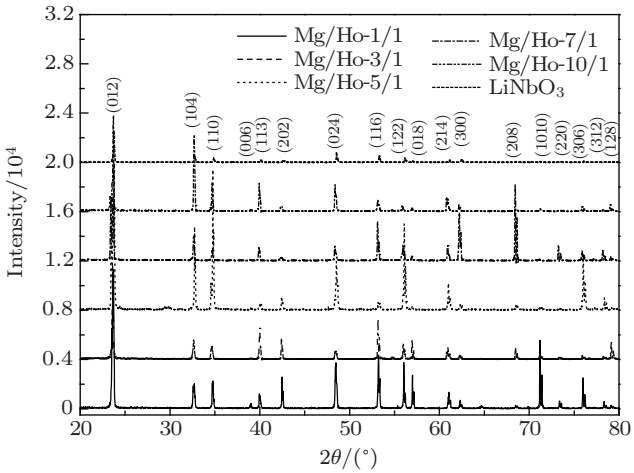


Fig. 2. X-ray powder diffraction patterns of Mg,Ho:$LiNbO_3$ crystal doped with Mg^{2+} (1 mol%)/Ho^{3+} (1 mol%), Mg^{2+} (3 mol%)/Ho^{3+} (1 mol%), Mg^{2+} (5 mol%)/Ho^{3+} (1 mol%), Mg^{2+} (7 mol%)/Ho^{3+} (1 mol%), and Mg^{2+} (10 mol%)/Ho^{3+} (1 mol%).

The threshold concentration for Mg doping was firstly reported to be 4 mol% by Zhong *et al.*[19]), both lattice constants and unit cell volume of crystals decrease. Mg^{2+} ions begin to enter into the normal Li and Nb sites to form Mg_{Li}^{+} and Mg_{Nb}^{3-} defects. The polarization ability of Mg^{2+} is better than that of Li^{+}, and the overlap extent of electronic clouds increases with the polarization ability of ions increasing, leading to the decrease of ionic radius. Hence, the cell parameter decreases.

Table 1. Lattice constants and unit cell volumes of the Mg:Ho:$LiNbO_3$ crystals.

Sample	a/Å	Δa/Å	c/Å	Δc/Å	V/Å^3	ΔV/Å^3	$\Delta R/10^{-5}$ cm^{-1}
$LiNbO_3$	5.1484	0	13.8382	0	317.65	0	0.8
Mg/Ho-1/1	5.1519	0.0035	13.8324	–0.0058	317.94	0.29	9.9
Mg/Ho-3/1	5.1533	0.0049	13.8350	–0.0032	318.17	0.52	8.4
Mg/Ho-5/1	5.1547	0.0063	13.8629	0.0247	318.99	1.34	6.6
Mg/Ho-7/1	5.1525	0.0041	13.8604	0.0222	318.66	1.01	2.7
Mg/Ho-10/1	5.1523	0.0039	13.8540	0.0158	318.49	0.84	1.1

3.2. Optical homogeneity

As is well known, the optical homogeneity of crystal is characterized by birefringence gradient ΔR. The larger the values of ΔR, the worse the optical uniformity of the crystal is, and vice versa. The birefringence gradient of the crystal is shown in Table 1. It is shown that the birefringence gradient ΔR of Mg,Ho:$LiNbO_3$ decreases with Mg^{2+} concentration increasing. This is because the increase of Mg reduces the segregation coefficient of Ho significantly.[20] Therefore, it is more difficult for the Ho ion to enter into the crystal lattice, which leads to the increase of the optical uniformity of the crystal.[21]

3.3. Upconversion spectrum

Upconversion spectrum under 808-nm femtosecond laser excitation is shown in Fig. 3. Five upconverted emission bands are observed to be centred at 425 nm (violet, medium), 486 nm (blue, medium), 561 nm (yellow–kelly, very strong), 656 nm (red, weak), and 725 nm (red, strong) originating from the $^5G_5 \rightarrow {}^5I_8$, $^5F_3 \rightarrow {}^5I_8$, $(^5S_2, {}^5F_4) \rightarrow {}^5I_8$, $^5F_5 \rightarrow {}^5I_8$, and $^5I_5 \rightarrow {}^5I_8$ transitions.[22]

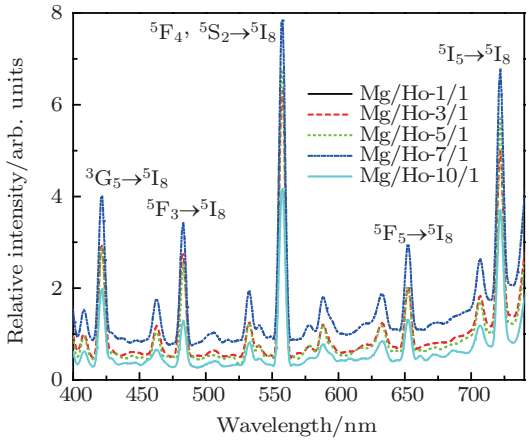


Fig. 3. (color online) Upconversion emission spectra of Mg,Ho:$LiNbO_3$ with various Mg concentrations under excitation at 808 nm. The emission bands are assigned in the figure.

Figure 4 displays the relationship between pump energy and upconversion emission of Ho^{3+} in Mg,Ho:$LiNbO_3$ crystal on the double logarithmic scale. To understand the upconversion mechanism, the pump power dependence of the fluorescent radiation is investigated. The number of photons responsible for the upper emitting state can be obtained by the relation[23]

$$I_f \propto P^n, \tag{2}$$

where I_f is the fluorescent intensity, P is the pump power, and n is the number of the laser photons required. The values of n are obtained from the slope of the graph of $\ln(I_f)$ versus $\ln(P)$. As it can be observed from Fig. 4, the value at lower pump power is close to 2, which indicates that this upconversion process is a two-photon process.[24]

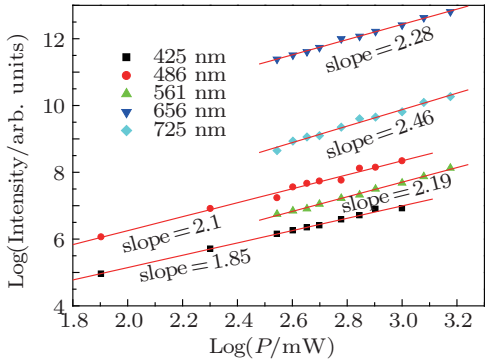


Fig. 4. (color online) Double logarithmic plot of the relationship between pump energy and upconversion emission integral intensities in Mg, Ho: $LiNbO_3$.

The energy levels of Ho^{3+} ion as well as the proposed two-photon upconversion mechanism are illustrated in Fig. 5. Under the 808-nm laser pump, the electrons of the Ho^{3+} ion transit from the ground state to the $^5I_5$ energy level. Once the electrons are excited by the 808-nm photons again, they transit from the $^5I_5$ to the $^5G_5$ level. At this time, some of the ions transit to the ground state via radiative transition, which produces 425-nm violet upconversion. The residual ions transit to the $^5F_3$, $^5F_4$, $^5S_2$, $^5F_5$, and $^5I_5$ levels via a set of quick nonradiative transitions. Finally, the electrons transit to the ground

state from the $^5F_3$, $^5F_4$, and $^5S_2$, $^5F_5$, $^5I_5$ levels via radiative transitions, and simultaneously produce the 486 nm, 561 nm, 656 nm, and 725 nm upconversion, respectively.

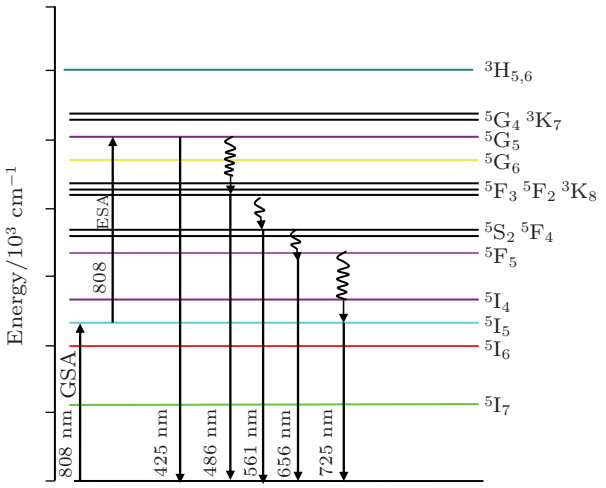


Fig. 5. (color online) Energy levels of Ho^{3+} ion as well as the proposed upconversion mechanism in Mg, Ho:$LiNbO_3$.

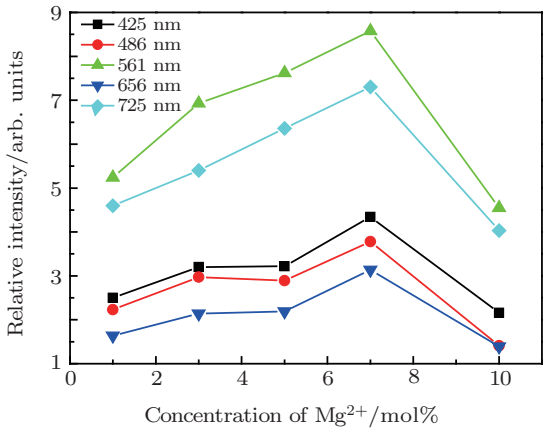


Fig. 6. (color online) Mg^{2+} concentration dependences of upconverted intensity of Mg, Ho: $LiNbO_3$ crystal doped with Mg^{2+} (1mol%)/Ho^{3+} (1 mol%), Mg^{2+} (3 mol%)/Ho^{3+} (1 mol%), Mg^{2+} (5 mol%)/Ho^{3+} (1 mol%), Mg^{2+} (7 mol%)/Ho^{3+} (1 mol%), and Mg^{2+}(10 mol%)/Ho^{3+} (1 mol%).

Figure 6 shows the dependences of upconverted intensity of samples on Mg^{2+} concentration under 808-nm excitation, in which we can see that with the increase of doping concentration of Mg^{2+}, the upconversion luminescence intensity of crystal increases. However, when the doping concentration of Mg^{2+} reaches 10 mol%, the upconversion luminescence will decline. Our results suggest that the increase of doping concentration of Mg^{2+} may be favourable for the location of electrons at the $^5G_5$, $^5F_3$, $^5F_4(^5S_2)$, $^5F_5$, and $^5I_5$ energy levels, thereby significantly increasing the spectrum transitions from them to the $^5I_8$ level. However, when the Mg^{2+} concentration reaches 10 mol%, the optimization distribution could not be held, and the spectrum transitions will decrease to some extent. This is because the incorporation of Mg^{2+} takes the place of Nb_{Li}^{4+}, forming an electron trap further reducing the rate of non-radiative transition of electrons, thus improving the luminescence environment of Ho^{3+}, and strengthening the radiation transition.

4. Conclusions

In this paper, a series of Mg,Ho:$LiNbO_3$ crystals with different concentrations of Mg ions are grown using the Czochralski technique. Under 808-nm femtosecond laser excitation, blue, violet, red, and very intense green bands are observed in Mg,Ho:$LiNbO_3$ crystals at room temperature. Five upconverted emission bands are assigned to the transitions $^5G_5 \rightarrow {}^5I_8$, $^5F_3 \rightarrow {}^5I_8$, $(^5S_2, {}^5F_4) \rightarrow {}^5I_8$, $^5F_5 \rightarrow {}^5I_8$, and $^5I_5 \rightarrow {}^5I_8$, respectively. It is concluded that this upconversion process is a two-photon process. The results obtained from the present study can promote the understanding of the relations between the Mg^{2+} concentration and the upconversion luminescence of Ho^{3+} ion in $LiNbO_3$ crystal, and they may be used directly to design and optimize such excellent materials.[25–28]

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