# $OH^-$ absorption and nonvolatile holographic storage properties in Mg:Ru:Fe:$LiNbO_3$ crystal as a function of Mg concentration*

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Mg:Ru:Fe:$LiNbO_3$ crystals with various concentrations of MgO (in mole) and fixed content of $RuO_2$ and $Fe_2O_3$ (in mass) are grown with the Czochralski method from the congruent melt. Their infrared transmission spectra are measured and discussed to investigate the defect structure. With the increase of $Mg^{2+}$ concentration the blue nonvolatile holographic storage capability is enhanced. The nonvolatile holographic storage properties of dual-wavelength recording of Mg(7 mol%):Ru:Fe:$LiNbO_3$ nonvolatile diffraction efficiency, response time, and nonvolatile sensitivity reach 59.8%, 70 s, and 1.04 cm/J, respectively. Comparing Mg(7 mol%):Ru:Fe:$LiNbO_3$ with Ru:Fe:$LiNbO_3$ crystal, the response time is shortened apparently. The nonvolatile diffraction efficiency and sensitivity are raised largely. The mechanism in blue photorefractive nonvolatile holographic storage is discussed.

**Keywords:** Mg:Ru:Fe:$LiNbO_3$ crystal, infrared spectroscopy, nonvolatile holographic properties

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## 1. Introduction

$LiNbO_3$ crystal is one of the most widely used nonlinear optical materials and has an important application in holographic volume storage, owing to its excellent photorefractive properties. The strong photorefractive effect in the crystal can be utilized in holographic storage, phase conjugation, optical calculation, and information processing.[1] However, several shortcomings of $LiNbO_3$ crystal, such as slow response speed, low sensitivity, strong photo-induced scattering, and volatility impede its practical applications in holographic storage. In the past few decades, doping different chemical elements into $LiNbO_3$ crystals to optimize the properties of the crystals has been attracting extensive attention.

Generally speaking, the impurities which can bring influence on the photorefractive effect of $LiNbO_3$ crystal can be roughly divided into two groups. One group is some metal ions with variable valency, such as Fe, Cu, and Mn.[2,3] Recently, studies demonstrated that a Ru ion can play a similar role.[4] This kind of dopant tends to enhance the photorefraction in the $LiNbO_3$ crystal. Usually, two kinds of these ions were incorporated into $LiNbO_3$ crystals in order to realize nonvolatile holographic storage, and Ru:Fe:$LiNbO_3$ was grown for this application.[5] Another group, including Mg, Zn, and Hf, has the ability to resist optical damage.[6–9] Among the dopants mentioned above, $Mg^{2+}$ dopant has been most widely investigated due to the high-quality Mg-doped $LiNbO_3$ crystal.[10] The relative minor ionic radius made it easy to grow the single crystal with large diameter and high optical quality. Recent studies revealed that the optical damage of some doped impurities depended on the incident laser wavelength. For instance, $LiNbO_3$ crystal-doped MgO showed strong optical damage resistance in the visible region; while in the ultraviolet range, the wavelength enhanced photorefractive effect was obtained.[11] However, almost all the experiments were carried out with a UV laser, and little attention was paid to the phenomenon under short-wavelength blue light irradiation.

In this paper, a series of $LiNbO_3$ crystals triply doped with Mg, Ru, and Fe is grown, and the blue nonvolatile holographic storage properties in these crystals are investigated by the dual-wavelength technique and two-color technique. The nonvolatile holographic storage properties of dual-wavelength recording are preferable to two-color recording under the same experimental conditions. Moreover, as $Mg^{2+}$ concentration increases, the nonvolatile holographic storage properties are enhanced. It is found that $Mg^{2+}$ ions are not scattering resistant at 476-nm wavelength and enhance the blue photorefraction.

## 2. Experiment

### 2.1. Crystal growth and sample preparation

$LiNbO_3$ crystals used in our experiments were grown in air with the Czochralski method from a congruent melt. The raw materials used in crystal growth were $Li_2CO_3$ (4N purity), $Nb_2O_5$ (4N purity), MgO (spectral purity), $RuO_2$ (spectral pu-

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rity), and $Fe_2O_3$ (spectral purity). The doping concentrations of $RuO_2$ and $Fe_2O_3$ were 0.10 and 0.03 wt.%, respectively. MgO concentrations in melt were 0, 1, 3, 5, and 7 mol%, respectively. All raw materials including $Li_2CO_3$, $Nb_2O_5$, MgO, $RuO_2$, and $Fe_2O_3$ were mixed for 24 h and were heated up to 750 °C for 2 h to remove $CO_2$, and then heated up further to 1100 °C for 2 h to form polycrystalline starting material with the aid of a solid-state reaction. The crystals were grown from the polycrystalline materials in a middle frequency heater furnace using a *c*-axis seed crystal. The raw material compositions and the optimum growth conditions for different samples are summarized in Table 1. After growth, the crystals were cooled to room temperature at a rate of 80 °C/h. All crystals exhibited good morphology and optical quality. It was found in HF-$HNO_3$ (1:2) etching experiments that multi-domain structures were found in all as-grown crystals. The crystals with multi-domain structures required a poling treatment prior to optical measurement and were placed into a furnace where the temperature gradient was below 3 °C/cm for polarization. After being held at a temperature of 1200 °C for 8 h, the crystal was polarized with a current density of 5 mA/cm$^2$. In the cool-down process, the temperature was reduced rapidly from 1000 to 800 °C to avoid the dissolved-off products. The crystals were cut into $20\times10\times2$ ($x\times z\times y$) mm$^3$ wafers and all sides were polished to optical quality. The *c* axis is along the longer edge. All samples were oxidized by annealing at 1000 °C in $O_2$ atmosphere.

**Table 1.** Doping concentration, growth condition, and crystal size of the sample.

| | $M_1$ | $M_2$ | $M_3$ | $M_4$ | $M_5$ |
|---|---|---|---|---|---|
| MgO concentration/mol% | 0 | 1.0 | 3.0 | 5.0 | 7.0 |
| $Fe_2O_3$ concentration/wt.% | 0.03 | 0.03 | 0.03 | 0.03 | 0.03 |
| $RuO_2$ concentration/wt.% | 0.10 | 0.10 | 0.10 | 0.10 | 0.10 |
| Temperature gradient/°C·cm$^{-1}$ | 40–50 | 40–50 | 40–50 | 40–50 | 40–50 |
| Pulling speed/mm·h$^{-1}$ | 2.00 | 2.00 | 1.20 | 0.80 | 0.20 |
| Rotation rate/r·min$^{-1}$ | 15–25 | 15–25 | 15–25 | 15–25 | 15–25 |
| Crystal size/mm$^2$ | $\phi30\times40$ | $\phi30\times40$ | $\phi30\times40$ | $\phi25\times30$ | $\phi25\times30$ |

### 2.2. Measurement

The infrared (IR) transmission spectra of the crystals were obtained with a Fourier IR spectrophotometer in a wavenumber range from 3400 cm$^{-1}$ to 3600 cm$^{-1}$ at room temperature.

The nonvolatile holographic storage properties of Mg:Ru:Fe:$LiNbO_3$ crystals were investigated by two-color recording. He–Ne laser (633 nm) and $Kr^+$ laser (476 nm) were used to record and sensitize light, respectively. A light beam from the He–Ne laser was split into two beams with a beam splitter, i.e., signal light S and reference R, both being polarized in the incidence plane. The two beams illuminated the *Y* plane of the crystal at an incident angle of $2\theta = 20^\circ$ during recording. The intensity of each beam was about 255 mW/cm$^2$. The grating vector was aligned along the *c* axis with a spacing period of 1.82 μm. The $Kr^+$ laser ($\lambda = 476$ nm) acted as sensitization light. Another method, named the dual-wavelength technique, was employed to measure the nonvolatile properties of the specimen, in which short and long wavelength lasers were used as recording and readout light, respectively. The two beams illuminated the *Y* plane of the crystal at an incident angle of $2\theta = 32^\circ$ during recording. The intensity of each beam was about 200 mW/cm$^2$.

## 3. Results and discussion

### 3.1. Infrared transmittance spectra

As shown in Fig. 1, in each of the $OH^-$ vibration bands of samples $M_1$, $M_2$, and $M_3$, there is an $OH^-$ absorption peak located at about 3482 cm$^{-1}$, while in each of the $OH^-$ vibration bands of samples $M_4$ and $M_5$, there is an $OH^-$ absorption peak located at 3535 cm$^{-1}$. The shape of the $OH^-$ absorption curve is related to the crystal composition and the ion surrounding of the $OH^-$.[12] The $OH^-$ absorption peak located at 3482 cm$^{-1}$ is a mark of congruent $LiNbO_3$ crystal. The $OH^-$ absorption peak at 3535 cm$^{-1}$ is a typical mark of $Mg^{2+}$ ions reaching the threshold value.[13]

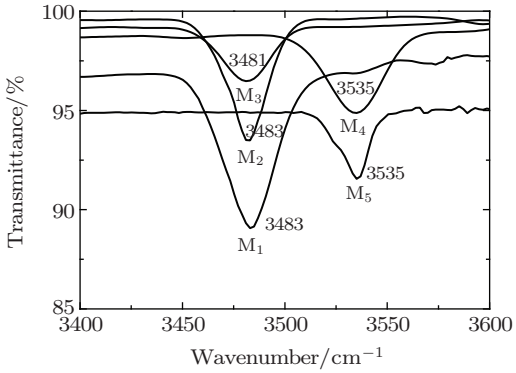



**Fig. 1.** Infrared transmittance spectra of Mg:Ru:Fe:$LiNbO_3$ crystals.

The mechanism of the absorption peak change is described as follows. In $LiNbO_3$ crystal, $H^+$ is confirmed to occupy the position on O–O bond. In congruent $LiNbO_3$ crystals, the [Li]/[Nb] ratio is approximately 0.94. Due to lack of Li ions in the crystal, the excess Nb ions will occupy Li sites to form anti-site Nb ($Nb_{Li}^{4+}$). At the same time, Li vacancy ($V_{Li}^-$) defects appear. The fact that $V_{Li}^-$ ions attract $H^+$ ions causes

$3V_{Li}^{-}Nb_{Li}^{4+}OH^{-}$ complexes which vibrate at 3482 $cm^{-1}$. When the concentration of $Mg^{2+}$ ions is below its threshold value, $Mg^{2+}$, $Ru^{4+}$, and $Fe^{3+}$ ions would replace $Nb_{Li}^{4+}$ ions to occupy Li sites and form $Mg_{Li}^{+}$, $Ru_{Li}^{3+}$, and $Fe_{Li}^{2+}$, respectively. These ions repel $H^{+}$ ions, so $H^{+}$ ions are still attracted by $V_{Li}^{-}$ ions. Therefore, $OH^{-}$ absorption peaks of samples $M_1$, $M_2$, and $M_3$ are still located in the proximity of 3482 $cm^{-1}$. When $Mg^{2+}$ ions reach or exceed a threshold value, they begin to replace $Nb^{5+}$ ions and occupy Nb site, forming $Mg_{Nb}^{3-}$, whose corresponding vibration peak is situated at 3535 $cm^{-1}$.[14,15]

### 3.2. Nonvolatile holographic storage

The resulting dual-wavelength nonvolatile holographic recoding-readout curves are shown in Fig. 2. The amplitude of maximal refractive index change ($\Delta n_s$) is calculated from maximal diffraction efficiency ($\eta_s$) according to Kogelnik formula $\Delta n_s = \lambda \cos\theta \arcsin\sqrt{\eta_s}/(\pi d)$, where $\lambda$ is the incident light wavelength in vacuum, $\eta_s$ the saturated diffraction efficiency, $d$ the effective interaction length, and $\theta$ the incident angle of laser beam within the crystal.[16] Considering the absorption of the crystal, the sensitivity of nonvolatile holographic recording can be represented by

$$S' = \beta S = \beta \frac{\mathrm{d}\sqrt{\eta_s}}{\mathrm{d}t}\bigg|_{t=0} \frac{1}{I_0 d},$$

where $\beta = \sqrt{\eta_f/\eta_s}$, $t$ is the time, $I_0$ the total recording light intensity, and $\mathrm{d}\sqrt{\eta}/\mathrm{d}t$ the rerecording slope defined as the initial time derivative of the square root of the diffraction efficiency.[17]

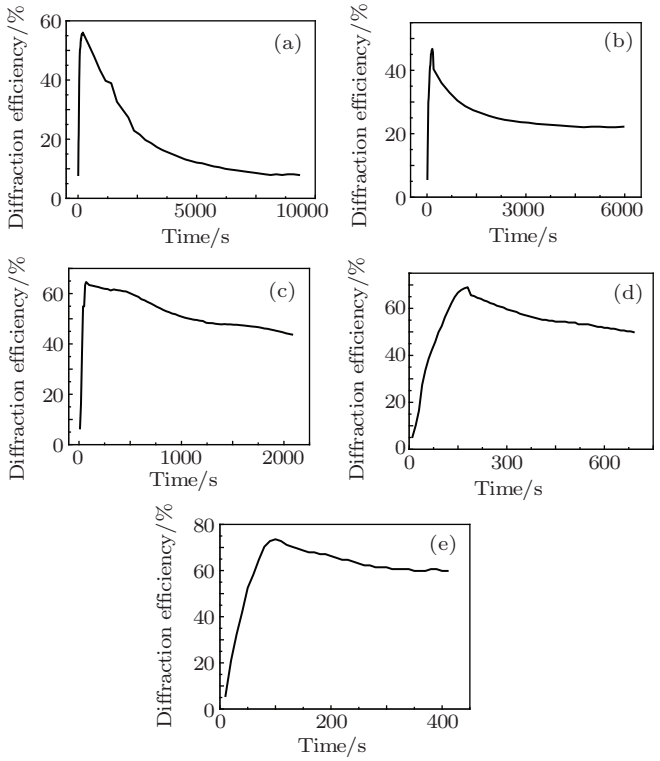



**Fig. 2.** Time dependences of diffraction efficiency during dual-wavelength recording for (a)–(f) samples $M_1$–$M_5$.

Tables 2 and 3 list the critical nonvolatile holographic parameters in dual-wavelength and two-color measurement. One can see that with the increase in $Mg^{2+}$ ion concentration, the properties are enhanced by dual-wavelength recording. Comparing Mg(7 mol%):Ru:Fe:$LiNbO_3$ ($M_5$) with Ru:Fe:$LiNbO_3$ ($M_1$), $\eta_s$ is increased by a factor of 1.3, $\eta_f$ by a factor of 7.6, $S'$ by a factor 52. At the same time, $\tau_w$ is shortened by a factor of 8.7. The nonvolatile diffraction efficiency $\eta_f$ and nonvolatile recording sensitivity $S'$ are the most important parameters in nonvolatile storage, and $\eta_f$ and $S'$ of sample $M_5$ reach their corresponding highest values. While for two-color nonvolatile experiment, the statured diffraction efficiency decreases with the increase in the doping concentration of MgO. In samples $M_3$, $M_4$, and $M_5$, we cannot obtain their nonvolatile readout. By simple comparison, one can easily find that dual-wavelength recording is a better method to realize nonvolatile storage.

**Table 2.** Parameters of dual-wavelength nonvolatile holographic recording.

| | $M_1$ | $M_2$ | $M_3$ | $M_4$ | $M_5$ |
|---|---|---|---|---|---|
| $\eta_s$/% | 56.1 | 46.8 | 64.2 | 69.0 | 73.6 |
| $\eta_f$/% | 7.8 | 22.0 | 43.7 | 49.9 | 59.8 |
| $\tau_w$/s | 610 | 180 | 160 | 100 | 70 |
| $\Delta n_s/10^{-5}$ | 0.353 | 0.314 | 0.387 | 0.408 | 0.431 |
| $S'$/cm·J$^{-1}$ | 0.02 | 0.22 | 0.36 | 0.63 | 1.04 |

**Table 3.** Parameters of two-color nonvolatile holographic recording.

| | $M_1$ | $M_2$ | $M_3$ | $M_4$ | $M_5$ |
|---|---|---|---|---|---|
| $\eta_s$/% | 28.5 | 19.0 | 14.2 | 11.5 | 10.5 |
| $\eta_f$/% | 15.0 | 14.0 | 0 | 0 | 0 |
| $\tau_w$/s | 995 | 580 | 320 | 145 | 98 |
| $\Delta n_s/10^{-5}$ | 0.319 | 0.255 | 0.166 | 0.144 | 0.186 |
| $S'$/cm·J$^{-1}$ | 0.054 | 0.074 | 0.120 | 0.240 | 0.324 |

The results above demonstrate that nonvolatile holographic storage properties in Mg:Ru:Fe:$LiNbO_3$ crystals are enhanced by dual-wavelength recording. It is well accepted that the nonvolatile holographic storage property of the Mg:Ru:Fe:$LiNbO_3$ crystal is dependent on its photorefractive sensitive centre. The Ru and Fe cations play the dominant roles. It is also known that the $Mg^{2+}$ cations do not participate in the charge transport process, and only contribute to the photoconductivity $\sigma_{ph}$. Doping $Mg^{2+}$ ions into the $LiNbO_3$ crystal will lead to an increased photoconductivity at 476 nm, resulting in a fast photorefractive response.[18] Here, holes are the dominant charge carriers under blue exposure.[19] It is found that the blue light is short enough to excite holes both in the shallow and deep trap centres, thus a grating can be directly recorded into the two centres. The repeating cycles of holes excitation-transport-trapping between shallow trap centre and deep trap centre are prohibited, therefore the sensitivity is enhanced compared with that in the conventional two-colour recording.[20] The gratings formed by both the shallow and

deep trap centres are in the same phase, thus the total diffraction intensity recorded from grating is the sum of diffraction intensities of the two gratings recorded in shallow and deep trap centres.[21] Therefore, the method of direct writing can enhance the nonvolatile properties dramatically. The diffraction intensity of the composite grating is raised obviously. Therefore, the method of direct writing enhances the resulting photorefractive effect dramatically. The factors mentioned above together contribute to the enhanced nonvolatile holographic properties by using dual-wavelength technology. Because $Mg^{2+}$ ions are not scatter resistant at 476 nm wavelength and they enhance the blue light photorefraction. Consequently, raising $Mg^{2+}$ ion concentration results in stronger photorefractive effect, and hence better nonvolatile holographic storage performance.

## 4. Conclusions

Mg:Ru:Fe:$LiNbO_3$ crystals are grown from the congruent melt with different concentrations of $Mg^{2+}$ ions. Their infrared transmittance spectra are measured and discussed in view of the defect structures. Using the dual-wavelength recording technique, it is demonstrated that the nonvolatile holographic storage properties are improved with the increase of $Mg^{2+}$ concentration largely. While in the two-color recording technique, nonvolatile holographic storage properties are degraded with the number of doping $Mg^{2+}$ ions increasing. In this case, $Mg^{2+}$ ions are not scatter resistant and thus the blue photorefractive effect is strengthened. For Mg(7 mol%):Ru:Fe:$LiNbO_3$ crystals, the highest fixing diffraction efficiency of 59.8% is achieved, which is a key parameter of great capacity volume holographic data storage, at the same time the nonvolatile sensitivity is as high as 1.04 cm/J. In a word, the Mg:Ru:Fe:$LiNbO_3$ crystals grown are promising in nonvolatile holographic storage.

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