# Nonvolatile photorefractive properties in triply doped stoichiometric Mg:Fe:Mn:$LiTaO_3$ crystals*

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We have grown triply doped Mg:Fe:Mn:$LiTaO_3$ crystals with near stoichiometry using the top seeded solution growth technique. The defect structure was investigated by infrared absorption spectra and Curie temperature. Using a blue laser as the source, excellent photorefractive properties were obtained. Nonvolatile holographic storage properties were investigated using the dual wavelength technique. We got a very high fixed diffraction efficiency and nonvolatile holographic storage sensitivity. The blue light has more than enough energy to excite holes of deep (Mn) and shallow (Fe) trap centers with the same phase, which enhance dramatically the blue photorefractive properties and the nonvolatile holographic storage. $Mg^{2+}$ ion is no longer damage resistant at blue laser, but enhances photorefractive characteristics.

**Keywords:** photorefractive material, $LiTaO_3$ crystal, nonvolatile holography, blue photorefraction

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## 1. Introduction

Ferroelectric single crystals have been widely used in optical communications, optical signal processing and holographic storage.[1–5] Lithium tantalate ($LiTaO_3$, LT) crystal was a useful material for nonlinear-optical, electro-optical and piezoelectric applications due to its high mechanical intensity, thermal stability and large electro-optical coefficients.[6] Fe:$LiTaO_3$ crystal has became one of the most important holographic storage media for industrial applications because of its high diffraction efficiency, high data storage density and long recording preservation time, long storage lifetime and so on.[7] However, three drawbacks exist, namely, the response time is too long, the optical damage resistance ability is too low and it cannot realize nonvolatile holographic storage. Therefore, Fe:$LiTaO_3$ crystals have been codoped optical-damage-resistant impurities, such as Mg, Zn, which can raise the optical damage resistant ability and the photorefractive sensitivity.[8,9] The photorefractive properties are also relevant to the incident light wavelength. Interband photorefraction in near-stoichiometric lithium tantalate has been demonstrated and investigated at the deep-ultraviolet (UV) wavelength $\lambda_{UV} = 257$ nm; typical time constants for the interband effects are of the order of a few tens of milliseconds for UV light intensities of approximately 100 mW/cm$^2$, three orders of magnitude faster than the time constants reported previously for lithium tantalate.[10] So far, almost all the enhanced photorefraction was investigated using UV light in pure or single element doped $LiTaO_3$ crystals, but little attention has been paid to the enhanced photorefraction in two sensitive-center doped $LiTaO_3$ crystals.[11,12] Moreover, the non-visibility or the radiation of UV light increases the difficulty and the danger in performing the experiment, which limit its applications in optical storage. Therefore, it is necessary to investigate the enhanced photorefraction of two sensitive-centre-doped $LiTaO_3$ crystals using a suitable short wavelength light in the visible region.

Based on the above consideration, the two-center Mg:Fe:Mn:S$LiTaO_3$ crystal was grown using the top seeded solution growth technique. The incident light wavelength was selected at 476 nm, which has enough energy to excite the carriers of Mg:Fe:Mn:S$LiTaO_3$ crystals. It is experimentally found that the blue photorefraction of the Mg:Fe:Mn:S$LiTaO_3$ crystals was enhanced dramatically by $Mg^{2+}$ ions. Nonvolatile photorefractive properties of Mg:Fe:Mn:S$LiTaO_3$ crystals were investigated using the dual wavelength technique. It is interesting that $Mg^{2+}$ ion is not damage resistant at the 476-nm wavelength, yet it enhances the blue photorefraction.

## 2. Experiment

Near-stoichiometric Mg:Fe:Mn:S$LiTaO_3$ crystals were grown using the top seeded solution growth technique (TSSG) in a melt of congruent composition [atomic ratio Li/(Ta+Li) $\approx$ 48.5%] containing 6-wt% $K_2O$. The Mg:Fe:Mn:S$LiTaO_3$

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crystals were grown along the $c$ axis with a congruent $LiTaO_3$ seed in the Pt crucible. The starting materials used for crystal growth were $Ta_2O_5$, $Li_2CO_3$, $K_2CO_3$, MgO, $Fe_2O_3$, and MnO. The fixed concentration of 0.075-wt% $Fe_2O_3$, 0.01-wt% MnO and various concentration of MgO (0 mol%, 0.5 mol%, 1 mol%, 1.5 mol%, 2 mol%) were added to the melt. The crystals with an increasing MgO concentration were denoted as LT0, LT0.5, LT1, LT1.5, and LT2. The Mg:Fe:Mn:SLiTaO$_3$ crystals were grown along the $c$ axis with congruent $LiTaO_3$ seeds in the Pt crucible. During the crystals growth, the temperature gradient above melt was 40 °C/cm–50 °C/cm, the pull speed was 0.2 mm/h–0.3 mm/h and the seed rotation rate was 15 rpm–25 rpm. For optical characterization and two-wave coupling experiments, the crystals were cut into crystal plates of 12 mm×10 mm×2 mm ($z \times x \times y$). All samples were polished to optical grade.

Infrared absorption spectra of the samples were measured at room temperature using a Nicolet-710FT-IR spectrometer in the wave number range from 3000 cm$^{-1}$ to 4000 cm$^{-1}$. The Curie temperature was measured by a differential scanning calorimeter (Model HT-DSC 404, Netzsch Instrument, Inc.). Transmittance spectra were measured as a function of the wavelength using a Perkin Elmer Lambda-900 UV-Visible-NIR spectrophotometer. The two-wave coupling experiment was used to investigate the photorefractive properties. A $Kr^+$ laser (476-nm blue light) was used as the light source to record and erase the holograms. The laser beam was split into two beams by a beam splitter, both being polarized in the incidence plane. The two beams illuminated the $y$ plane of the crystal, whose crossing angle was $2\theta = 32°$ during recording. The intensity of each beam was about 100 mW/cm$^2$. For comparison, the photorefractive properties at 633-nm laser were measured using the same optical setup with a He–Ne laser.

Experimental optical path for nonvolatile holographic storage is shown Fig. 1. A shorter wavelength light ($\lambda$ = 476 nm) was used as the recording light, a longer wavelength light as ($\lambda = 633$ nm) the read out light, which is called the dual wavelength technique.[13]

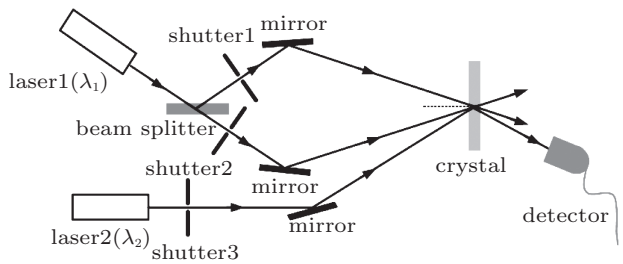



**Fig. 1.** Experimental setup for nonvolatile holographic storage of the dual wavelength technique, where $\lambda_1 = 476$ nm, $\lambda_2 = 633$ nm.

## 3. Results and discussion

### 3.1. Infrared absorption spectra

The infrared absorption spectra of the Mg:Fe:Mn:SLiTaO$_3$ crystals is shown in Fig. 2. The positions of the $OH^-$ vibration absorption peak locate at 3459 cm$^{-1}$, 3473 cm$^{-1}$, 3496 cm$^{-1}$, 3511 cm$^{-1}$, and 3527 cm$^{-1}$. In the $OH^-$ vibration band of LT0, there is one absorption peak located at 3459 cm$^{-1}$ (Li–$OH^-$ vibration), which is a mark of stoichiometric $LiTaO_3$ crystals.[8,14] LT0 may be pure stoichiometric $LiTaO_3$ crystals. In the $OH^-$ vibration band of LT0.5, there are two absorption peaks located at 3459 cm$^{-1}$ and 3473 cm$^{-1}$; the absorption peak located at 3473 cm$^{-1}$ is a satellite of 3459 cm$^{-1}$. $Mg^{2+}$ ion in LT0.5 reaches 0.5 mol%, $Mg^{2+}$ ion replaces the $Li^+$ ion and results in the increase of $V_{Li}^-$ concentration, $V_{Li}^-$ attracts $H^+$ ion forming $V_{Li}$–$OH^-$ complexes vibration at 3473 cm$^{-1}$. Therefore, LT0.5 is near-stoichiometric $LiTaO_3$ crystals. In the $OH^-$ vibration band of LT1, there are three absorption peaks located at 3496 cm$^{-1}$, 3511 cm$^{-1}$, and 3527 cm$^{-1}$. In LT1, $Mg^{2+}$ ion concentration increases to 1 mol%, which raises the $V_{Li}^-$ concentration simultaneously. The high doing $Mg^{2+}$ ion destroys the stoichiometric structure of $LiTaO_3$ crystals. $Mg^{2+}$ ion reaches the threshold value, since it replaces $Ta^{5+}$ ions forming a $Mg_{Ta}^{3-}$ ion, which results in $Mg_{Ta}^{3-}$–$OH^-$ complexes vibration at 3527 cm$^{-1}$.[15,16] The doping elements Fe and Mn change their occupation from Li-sites to Ta-sites; the absorption peaks located at 3496 cm$^{-1}$ and 3511 cm$^{-1}$ may be due to the $Mg_{Li}^{+}$–$OH^-$–$Fe_{Ta}^{2-}$ and $Mg_{Li}^{+}$–$OH^-$–$Mn_{Ta}^{3-}$ bandings.[12] When the $Mg^{2+}$ ion concentration reaches 2 mol% and 3 mol%, in LT1.5 and LT2 there is only one absorption peak at 3527 cm$^{-1}$, which corresponds to $Mg_{Ta}^{3-}$–$OH^-$ complexes vibration.

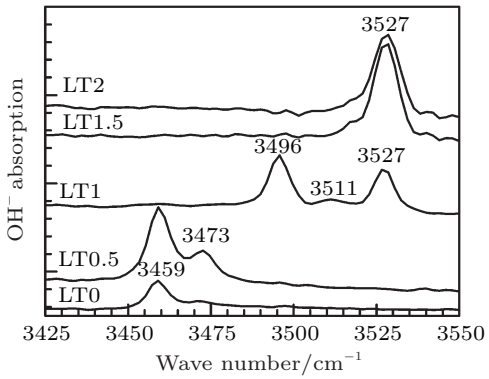



**Fig. 2.** Infrared absorption spectra of Mg:Fe:Mn:SLiTaO$_3$ crystals.

### 3.2. Curie temperature

Figure 3 shows the dependence of the Curie temperature on $Mg^{2+}$ ion doping concentration, from which we can see that the Curie temperature goes up with the increase in the concentration of $Mg^{2+}$ ions when it is below 1 mol%. The Curie temperature, however, decreases with the increase

in the concentration of $Mg^{2+}$ ions when the concentration is above 1 mol%. The doping concentration of $Mg^{2+}$ ions influences the Curie temperature significantly. The concentration of $Mg^{2+}$ ions changes from 0 mol% to 1 mol%, the Curie temperature increases 11 °C. The degree of stoichiometry of the grown crystals can be estimated by the Curie temperature $T_c$, since this temperature depends strongly on stoichiometry.[10] The Curie temperature of congruent crystals is $T_c \sim 601$ °C and for sintered powders of exact stoichiometric composition $T_c \sim 692$ °C. By assuming a linear relationship between $T_c$ and the crystal composition, we can estimate the degree of stoichiometry that is given by the Li/(Ta+Li) atomic ratio is 48.5% for congruent-melt crystals and 50% for perfect stoichiometric crystals.

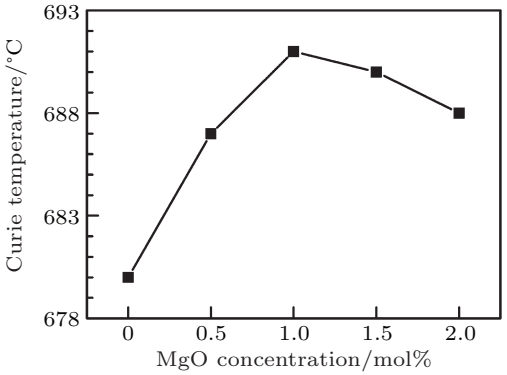



**Fig. 3.** $Mg^{2+}$ ion concentration dependence of Curie temperature in Mg:Fe:Mn:SLiTaO$_3$ crystals.

### 3.3. Blue photorefractive properties

The transmission spectra of Mg:Fe:Mn:SLiTaO$_3$ crystals are shown in Fig. 4. For all the crystals, the transmittance begins to increase abruptly at around 300 nm, which indicates an optical absorption edge in the ultraviolet region. The curves rise near 350 nm; these crystals are transparent in visible and near IR spectral regions.

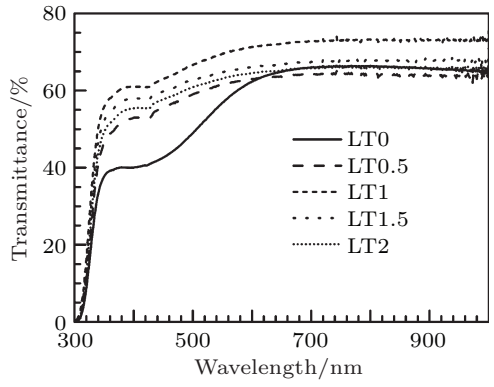



**Fig. 4.** Transmittance spectra of Mg:Fe:Mn:SLiTaO$_3$ crystals.

If the energy transfer direction is the same to the $+c$ axis of the crystals, the dominant charge carrier can be determined as a hole. Otherwise, the dominant charge carrier is electron.[17] The dominant charge carrier trapped in blue ($\lambda = 476$ nm) photorefraction is identified as a hole, since the direction of the two-wave mixing gain is toward the positive poling electrode's $c$ face. On the contrary, the dominant charge carrier trapped in red ($\lambda = 633$ nm) photorefraction is identified as an electron.

The photorefractive properties of Mg:Fe:Mn:SLiTaO$_3$ crystals were measured using a $Kr^+$ laser ($\lambda = 476$ nm). The maximal diffraction efficiency of the grating is $\eta_s = I_d/(I_d + I_t)$, where $I_d$ and $I_t$ are the diffracted and transmitted light intensities. For holographic storage systems, two most important system parameters are the dynamic range ($M/\#$) and sensitivity ($S$). The larger $M/\#$, the higher storage density and the better the signal-to-noise ratio will be. The sensitivity $S$ determines the recording speed. Both of them can be obtained via the time dependence of the diffraction efficiency during the recording-erasing process, which is the same as the method to measure $M/\#$.

The dynamic range $M/\#$, sensitivity $S$, and maximal refractive index change $\Delta n_s$ can be calculated with[18–20]

$$M/\# = \tau_e \left( \frac{d\sqrt{\eta}}{dt} \right)_{t=0} \approx \frac{\tau_e \sqrt{\eta_s}}{\tau_w}, \tag{1}$$

$$S = \frac{(d\sqrt{\eta}/dt)_{t=0}}{IL} \approx \frac{\sqrt{\eta_s}}{\tau_w IL}, \tag{2}$$

$$\Delta n_s = \frac{\arcsin\sqrt{\eta_s}\lambda \cos\theta}{\pi L}, \tag{3}$$

where $\eta_s$ is the maximal diffraction efficiency, $\tau_w$ and $\tau_e$ are the recording and erasing time constants, $I$ is the total recording intensity, $L$ is the thickness of the wafer, $\lambda$ is the laser wavelength in free space and $\theta$ is the incident angle inside the crystal. The experimental results are summarized in Table 1.

**Table 1.** Photorefractive properties of Mg:Fe:Mn:SLiTaO$_3$ crystals at 476 nm.

| Crystal | $\tau_w$/s | $\tau_e$/s | $\eta_s$/% | $M/\#$ | $S$/(cm/J) | $\Delta n_s/10^{-5}$ |
|---|---|---|---|---|---|---|
| LT0 | 68 | 282 | 62.5 | 3.27 | 0.409 | 0.426 |
| LT0.5 | 62 | 245 | 65.4 | 3.19 | 0.459 | 0.446 |
| LT1 | 51 | 231 | 68.3 | 3.74 | 0.472 | 0.454 |
| LT1.5 | 44 | 146 | 71.6 | 2.80 | 0.677 | 0.471 |
| LT2 | 38 | 125 | 76.3 | 2.87 | 0.810 | 0.497 |

From Table 1, we can see the excellent photorefractive properties of Mg:Fe:Mn:SLiTaO$_3$ crystals. $\eta_s$, $M/\#$, and $S$ reach 76.3%, 3.74, and 0.810 cm/J, respectively. From LT0 to LT2, $\eta_s$ gradually increases. Whereas using 633-nm red light as the source, $\eta_s$ gradually decreases from LT0 to LT2.

### 3.4. Nonvolatile holographic storage

Experimental results of nonvolatile holographic recording and erasing are shown in Fig. 5. Considering the absorption of

crystals, the sensitivity of nonvolatile holographic recording sensitivity can be represented as

$$S' = \beta \frac{\mathrm{d}\sqrt{\eta}}{\mathrm{d}t}\bigg|_{t=0} \frac{1}{I_0 d}, \tag{4}$$

where $I_0$ is the total recording light intensity, $\beta = (\eta_\mathrm{f}/\eta_\mathrm{s})^{1/2}$ is a fixed factor, $\eta_\mathrm{f}$ is the fixed diffraction efficiency and $\eta_\mathrm{s}$ is the maximal diffraction efficiency.[21] Experimental results are shown in Table 2. We can see that large $\eta_\mathrm{s}$ (72.0%), $\eta_\mathrm{f}$ (62.5), and $S'$ (0.335 cm/J) are obtained. Large $\eta_\mathrm{f}$ and $S'$ are important targets of great capacity volume holographic storage. Nonvolatile holographic storage sensitivity is as great as 0.198 cm/J–0.335 cm/J, which is one-order greater than that of stoichiometric $LiTaO_3$ or Mg:Fe:$LiTaO_3$ crystals.[12,16] Fixing diffraction efficiency $\eta_\mathrm{s}$ is more than six-times greater than that of near-stoichiometric $LiTaO_3$ crystals doped with Mn.[22–29]

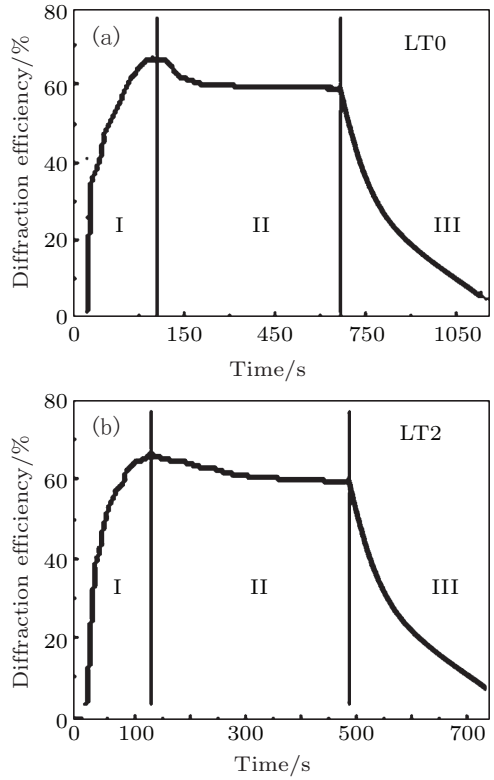



**Fig. 5.** Experimental curve of dual wavelength recording nonvolatile storage properties of (a) LT0 and (b) LT2. Region I: record with one red and two blue beams, region II: readout with one red light and region III: erase with one blue light.

**Table 2.** Nonvolatile holographic storage properties of Mg:Fe:Mn:SLi$TaO_3$ crystals by dual wavelength recording.

| Crystal | $\eta_\mathrm{s}$/% | $\eta_\mathrm{f}$/% | $\tau_\mathrm{w}$/s | $S$/(cm/J) | $S'$/(cm/J) |
|---|---|---|---|---|---|
| LT0 | 62.5 | 59.0 | 105 | 0.210 | 0.198 |
| LT0.5 | 64.6 | 59.5 | 95 | 0.235 | 0.216 |
| LT1 | 67.8 | 60.5 | 83 | 0.275 | 0.221 |
| LT1.5 | 70.1 | 61.0 | 72 | 0.323 | 0.281 |
| LT2 | 72.0 | 62.5 | 61 | 0.386 | 0.335 |

Photorefractive properties of the doped $LiTaO_3$ crystals depend mainly on its photorefractive sensitive centers. In the Mg:Fe:Mn:SLi$TaO_3$ crystals, Fe and Mn play the dominant role. The Fe trap has shallow trap centers, while the Mn trap has deep trap centers under blue light irradiation. The blue light is short enough to excite holes in both shallow and deep trap centers, thus a grating can be directly recorded into the two sensitive centers with the same phase. The total intensity of the recorded grating is the sum of the two gratings recorded in deep and shallow trap centers. Therefore, the photorefractive characteristics are improved dramatically compared with those in single

sensitive-center-doped $LiTaO_3$ crystals at a wavelength of 476 nm. The $Mg^{2+}$ ions do not participate in the charge transport process, but they can affect the concentration and the occupation of other ions. $Mg^{2+}$ ions contribute to the photoconductivity $\sigma_\mathrm{ph}$, thus result in sensitivity enhancement.

## 4. Conclusion

The near-stoichiometric Mg:Fe:Mn:SLi$TaO_3$ crystals were grown using the TSSG technique with 6 wt% $K_2O$ as the flux. Using IR transmission spectra and Curie temperature of crystals, the defect structure and the threshold concentration in crystals were investigated; 1 mol% MgO in Mg:Fe:Mn:SLi$TaO_3$ crystals reaches the threshold value, whereas 5-mol% MgO in congruent Mg:$LiTaO_3$ crystals reaches the threshold value. Holes are the dominant charge carriers in crystals at blue light recording. The wavelength of the blue light is short and its energy is large enough to excite the holes of shallow and deep trap centers. The photorefractive properties of the Mg:Fe:Mn:SLi$TaO_3$ crystals were investigated experimentally at a wavelength of 476 nm. The blue photorefraction is enhanced significantly. The $\eta_\mathrm{s}$, $\tau_\mathrm{w}$, $M/\#$, and $S$ of LT2 reach 76.3%, 38 s, 2.87, and 0.810 cm/J, respectively. The nonvolatile holographic storage of the dual wavelength technique was investigated by a $Kr^+$ laser (476-nm blue light) as the recoding light. The $\eta_\mathrm{f}$ and $S$ of the dual wavelength technique reach 62.5% and 0.386 cm/J.

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