Photorefractive properties of iron-doped stoichiometric lithium niobate

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The photorefractive properties of stoichiometric LiNbO₃ crystals with a small number of defect densities grown by the double-crucible Czochralski method are investigated and compared with the defect densities of commercially available congruent Fe-doped LiNbO₃ crystals. Two-wave-mixing experiments show that novel stoichiometric crystals exhibit larger photorefractive gain and considerably faster response times than congruent ones. The results indicate that the nonstoichiometry defect control of photorefractive crystals is of key importance for the improvement of their properties. © 1997 Optical Society of America

Lithium niobate (LiNbO₃; LN) single crystals have been well studied as a material for volume holographic memory applications because of their good mass productivity and excellent photorefractive properties such as long storage time and relatively high coupling gain constant. Fe-doped LN crystals investigated in the past had a congruent composition and contained a considerably large amount of intrinsic defects at a particular lattice site as a result of nonstoichiometry; these defects level are larger by 2 or 3 orders of magnitude than ordinary Fe-dopant-concentration levels. This is because the growth of bulk LN crystal with stoichiometric composition by the conventional Czochralski method is very difficult, since LN is an oxide compound that exhibits wide nonstoichiometry in the Li/Nb cation ratio. However, two different recent developments of crystal-growth technique yielded high-quality bulk-stoichiometric LN and have opened the field for further investigations and applications. Kitamura reported that stoichiometric LN can be grown from congruent melt with 6 wt. % K₂O added to it. Recently, Jerman and co-workers investigated photorefractive properties of congruent and stoichiometric LN at very high light intensities and reported that light-induced birefringence changes in the congruent sample are much larger than in the stoichiometric crystal, whereas at less than 2 MW/cm² the values of stoichiometric LN are higher. They proposed a two-center charge-transfer model for Fe-doped LN to explain their experimental results. In this Letter we investigate the influence of nonstoichiometricity on the photorefractive properties of LN at low light intensity (1–10 W/cm²) and report that stoichiometric LN crystals grown by the DCCZ method show enhanced photorefractive gain and response compared with Fe-doped congruent LN.

We grew optical-quality Fe-doped stoichiometric LN crystals from melt with 58 mol. % Li₂O by the DCCZ method, using an automatic powder supply system that was developed to overcome the difficulties in high-homogeneity crystal growth by the conventional Czochralski method and to control precisely the [Li]/[Nb] ratio and the defect density in crystal. The maximum size of stoichiometric LN grown so far, using the DCCZ system, was 55 mm in diameter, 140 mm in length, and ~850 g in weight. The crystal composition over the whole diameter and over the whole length of crystal grown was estimated to be stoichiometric from both its chemical analysis and its Curie temperature, calculated with the equation proposed by O’Bryan et al. Fe concentration in the doped crystal was analyzed to be homogeneous by the ion-coupling-plasma method. It was found in the etching experiments that the as-grown crystals obtained by this method exhibited a single ferroelectric domain structure except at the periphery of the bouls. The samples used for optical characterization were cut from the single-domain area and polished into a y plate with a size of 10 mm × 10 mm and 2 mm in thickness. More details of crystal growth are reported in Ref. 7.

Figure 1 shows the absorption spectra for stoichiometric LN and congruent LN. Stoichiometric LN exhibits a shift of the absorption edge toward a shorter wavelength, from 322 to 305 nm at α = 15 cm⁻¹. Introduction of a certain amount of Fe dopant results in an effective absorption band in the visible region, centered around 460 nm.

To compare photorefractive properties between stoichiometric and congruent LiNbO₃ crystals, we performed two-wave-mixing experiments, using a frequency-doubled Nd:YAG laser with a 532-nm wavelength at a grating period of 1.6 μm. The total beam intensity was a range from 1 to 10 W/cm² with a pump–signal intensity ratio of 100. By measuring I₀, the signal-beam intensity after the beam passes through the crystal, with and without reference beams, we found that the amplification γ was...
The exponential gain coefficient $\Gamma$ can be obtained through the equation:\(^\text{(2)}\)

$$\Gamma = 1/L \ln[(m \gamma)/(1 + m - \gamma)],$$

where $m$ is the pump–signal intensity ratio and $L$ is the interaction length of two incident beams in the crystal. The time dependence of the exponential gain coefficient $\Gamma(t)$ was used to obtain the characteristic photorefractive buildup time of the material.

Figures 2 and 3 summarize the experimental results for the exponential gain coefficient and the buildup time, respectively, for various samples. We found a maximum gain coefficient of $\Gamma = 15 \text{ cm}^{-1}$ for Fe-doped congruent LiNbO$_3$. In nondoped congruent LiNbO$_3$, in contrast, a negligibly small amplification is observed. The best results were obtained in the stoichiometric samples. We measured a maximum gain coefficient of $\Gamma = 27 \text{ cm}^{-1}$ in Fe-doped stoichiometric LiNbO$_3$, but even nondoped stoichiometric samples exhibited a large exponential gain of $25 \text{ cm}^{-1}$. The increase of nonlinearity in the stoichiometric samples does not come at the expense of response time. On the contrary, our experiments show that the buildup time in the stoichiometric samples is $\sim 10$ times faster than in the congruent ones, as shown in Fig. 3. In view of this significant increase in photorefractive sensitivity, optimized stoichiometric LN crystals may hold much promise for hologram data-storage applications. Therefore understanding and controlling the photorefractive parameters of this crystal are of great importance.

The exponential gain coefficient and the response speed of Fe-doped stoichiometric LN for various annealing conditions was also investigated. The average value of the exponential gain coefficient of Fe-doped stoichiometric LN is $\sim 22 \text{ cm}^{-1}$; this value rarely depends on either incident beam intensity or annealing condition, but the buildup time strongly decreases with the increase of total beam intensity and reduction of samples, as shown in Fig. 4. The response time of 270 parts in $10^6$ (ppm) of Fe-doped stoichiometric LN crystals with reduced annealing condition depends linearly on the incident beam intensity as $\sim 5 \times I^{-1.0}$.

The Fe-dopant-concentration dependence on the photorefractive gain and the response of the stoichiometric LN are shown in Figs. 5 and 6, respectively. One of the notable features of nondoped stoichiometric LN crystals is that they show a wide variation of exponential gain coefficient with different sample annealing conditions, even though some of them show a large gain coefficient such as $25 \text{ cm}^{-1}$. This may be because the grating spacing where this measurement was performed was not trap limited; thus gain was sensitive

![Fig. 2. Maximum exponential gain coefficient $\Gamma$ for stoichiometric and congruent LN crystals with reduced annealing conditions. Two-wave mixing was performed at $\lambda_g = 1.6 \mu \text{m}$ and $I_0 = 10 \text{ W/cm}^2$.](image)

![Fig. 3. Photorefractive response time $\tau$ for stoichiometric and congruent LN crystals with reduced annealing conditions. Two-wave mixing was performed at $\lambda_g = 1.6 \mu \text{m}$ and $I_0 = 10 \text{ W/cm}^2$.](image)

![Fig. 4. Photorefractive buildup time $\tau$ of 270 ppm of Fe-doped stoichiometric LN at $\lambda_g = 1.6 \mu \text{m}$ for various annealing conditions as a function of incident beam intensity.](image)
Fig. 5. Exponential gain coefficient of stoichiometric LN versus Fe-dopant concentration for various annealing conditions at $\Lambda_g = 1.6 \, \mu m$ and $I_0 = 10 \, W/cm^2$.

Fig. 6. Photorefractive buildup time $\tau$ versus Fe-dopant concentration for reduced stoichiometric LN at $\Lambda_g = 1.6 \, \mu m$.

only to dopant concentration. On the contrary, starting with 140 ppm of Fe-doped crystals, we note that the fluctuation of the gain coefficient is smaller and remains at high values of from 19 to 27 cm$^{-1}$. The important characteristic of Fe doping into stoichiometric LN is that it improves photorefractive response speed more than 10 times while maintaining large gain. The biggest advantage of stoichiometric LN is that a large amount of Fe doping is not necessary to improve photorefractive properties, while for congruent crystals more than 300 ppm of Fe doping is needed to increase photorefractive properties, and this is not desirable for practical application because a large amount of Fe absorbs a large amount of incident laser light.

We characterized the erasure time of grating by monitoring the power decay of diffracted reference light with the signal beam blocked after the two-wave mixing. For both Fe-doped stoichiometric and congruent crystals, power decays exponentially with time, and erasure speed depends almost linearly on the intensity of the incident light. For a given intensity, the time required for erasure of the grating is as much as 3 to 5 times longer than the time required to write a photorefractive grating.

These facts leads to the speculation that, although the nonstoichiometric defects essentially are related to the photorefractive effects in LN, too large a density of the defects, e.g., a few percent, at a particular lattice site in the congruent LN suppresses the photorefractive effect. To understand fully the behavior of the large gain and the faster response of stoichiometric LN than congruent crystals, quantitative study for the photovoltaic effects and fanning should be investigated as a function of nonstoichiometric defects.

In summary, we have reported on the absorption coefficient, two-beam exponential gain coefficient, and photorefractive response time of Fe-doped stoichiometric LN crystals grown by the double-crucible Czochralski method from melt with 58.0 mol. % Li$_2$O. Stoichiometric LN showed enhanced photorefractive properties such as larger gain and considerably faster response speed compared with the commercially available Fe-doped congruent LN grown from melt with 48.6 mol. % Li$_2$O. The results obtained are clear evidence that nonstoichiometric defect control of photorefractive crystals is of key importance for the improvement of their properties.

References