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Growth and Property of Stoichiometric $LiNbO_3$ Crystal†

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Near-stoichiometric $LiNbO_3$ and Fe:$LiNbO_3$ were grown. The ultraviolet-visible absorption spectra, infrared absorption spectra, exponent gain coefficient, diffraction efficiency and response time of these crystals were measured. It is found that the response time of Near-stoichiometric $LiNbO_3$ and Fe:$LiNbO_3$ was one order of magnitude less than that of congruent $LiNbO_3$.

Keywords: $LiNbO_3$ crystal; absorption spectrum; exponent gain coefficient

INTRODUCTION

$LiNbO_3$ crystal is electro-optic crystal with perfect electro-optic property and nonlinear optical property. It is used in many fields as a kind of important photorefractive material. That there are many intrinsic defects in the crystal are the main shortcomings of the congruent $LiNbO_3$ crystal [1]. The near-stoichiometric $LiNbO_3$ has much less intrinsic defects than the congruent $LiNbO_3$. So the photorefractive ability of the near-stoichiometric $LiNbO_3$ is higher than that of the congruent $LiNbO_3$.

EXPERIMENTAL PROCEDURES AND RESULTS

The Growth of Crystals

Czochralski method was used to grow $LiNbO_3$ crystal and Fe:$LiNbO_3$ crystal. The raw materials using to grow crystals were Li_2CO_3, Nb_2O_5 and Fe_2O_3

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with purity of 99.99%. The ratio of $[Li_2CO_3]$ to $[Nb_2O_5]$ was 1.44. $[Fe_2O_3]$ was 0.03 mol%. The growth orientation was c-axis. The optimized technology conditions of crystal growth were that the temperature gradient was $30 \sim 40$°C/cm, the rotating rate was $20 \sim 30$ rpm, and the pulling rate was 0.2 mm/h. The crystals were made into samples after being cut and polished, which dimension was $10 \times 5 \times 1\ mm^3$.

Ultraviolet-Visible Absorption Spectra of $LiNbO_3$ Crystals

The ultraviolet-visible absorption spectra of congruent $LiNbO_3$ and near-stoichiometric $LiNbO_3$ were measured by using CARYIE style UV-Visible Spectrophotometer. The results was shown in Fig. 1.

The absorption edges of congruent LN and near-stoichiometric crystals spectra located at 320 nm and 306 nm, respectively. The relation of the wavelength (λ) of the absorption edge with the concentration (χ) of Li^+ could be described by the following equation [2]

$$\lambda = 321.9 - 1.597\chi - 5.745\chi^2 \tag{1}$$

From the last equation, the concentration of 49.6 mol% of Li^+ in congruent $LiNbO_3$ was obtained. Because there are much less intrinsic defects in the near-stoichiometric $LiNbO_3$ than in the congruent $LiNbO_3$, i.e. the polarizing degree of O^{2-} was decreased, compared with the absorption edge of the congruent $LiNbO_3$, that of near-stoichiometric $LiNbO_3$ shifted to the ultraviolet band.

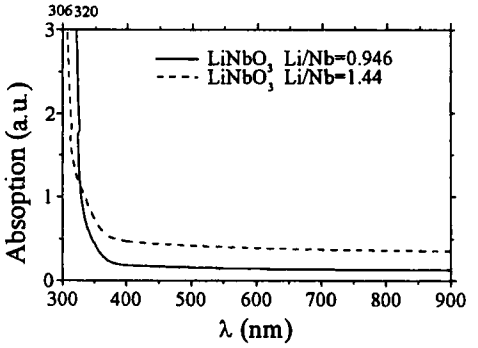

Figure 1. The ultraviolet-visible absorption spectra of congruent LN and near-stoichiometric crystals.

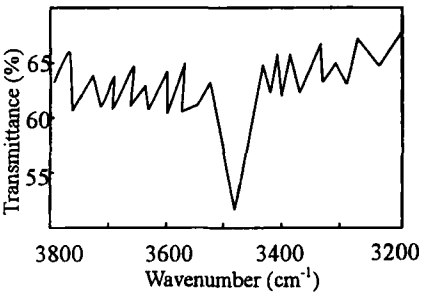

Figure 2. The infrared absorption spectrum of the congruent $LiNbO_3$.

Infrared Absorption Spectra of $LiNbO_3$ Crystals

The infrared absorption spectra of the congruent and the near-stoichiometric $LiNbO_3$ crystals were measured by Fourier conversion infrared spectrophotometer and the results were shown in Figs. 2 and 3, respectively.

For $LiNbO_3$ crystals, the position of the OH^- absorption peak was affected by OH_{Li} (H^+ occupied the Li^+ site). The main form of the intrinsic defect was Li vacancy (V_{Li+}) and antisite Nb (Nb_{Li}^{4+}, Nb^{5+} occupied the Li^+ site). The defect structure group that one Nb_{Li}^{4+} was connected with its nearest four Li vacancies made the charge balance in the crystal. The stretch vibrations of the defect structure group and OH^- were corresponding to the peak that was located at 3483 cm^{-1}.

Exponential Gain Coefficient Measurements [3]

The exponential gain coefficient of the photorefractive crystal is corresponding to the energy transition from the pump light to the signal light during the information storage process. The larger the exponential gain coefficient

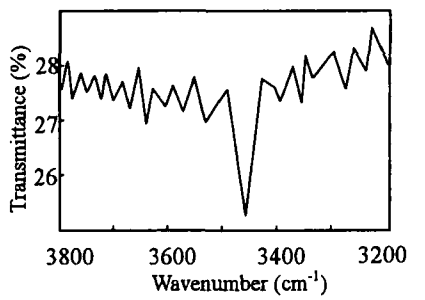

Figure 3. The infrared absorption spectrum of the near-stoichiometric LiNbO.

TABLE I The exponential gain coefficients of crystals

Crystal	2θ	Γ_{max} (cm^{-1})
Near-stoichiometric Fe:$LiNbO_3$	32°	43
Near-stoichiometric $LiNbO_3$	23°	24
Congruent $LiNbO_3$	10°	9.5

is, the more multiple the signal light is amplified. The exponential gain coefficient Γ was defined as

$$\Gamma = \frac{1}{\delta} \ln \frac{I_1' I_2}{I_1 I_2'} \approx \frac{1}{\delta} \ln \frac{I_1'}{I_1} \tag{2}$$

where I_1' and I_2' (I_1 and I_2) are the transmitted intensities of signal beam and pumping beam with (without) coupling, respectively. The exponential gain coefficients of the reduced samples of the near-stoichiometric Fe:$LiNbO_3$, near-stoichiometric $LiNbO_3$ and congruent $LiNbO_3$ were measured with the two-wave coupling method. The results were shown in Table I.

Diffraction Efficiency and Response Time Measurements

The diffraction efficiency of crystals was measured by two-wave coupling method. Ar^+ laser with wavelength of 514.5 nm was used, which intensity was 1.34 W/cm^2. The measurement results were shown in Table II. The response time is defined as the time period that is from the time of the incident light beginning to shot on the crystal to the time when the diffraction efficiency reaches its maximum. The measurement results were shown in Table II.

TABLE II The diffraction efficiency and response time of crystals

Crystal	2θ	η_{max}	t (s)
Near-stoichiometric Fe:$LiNbO_3$	20.5°	70%	5.6
Near-stoichiometric $LiNbO_3$	33°	42%	1.5
Congruent $LiNbO_3$	9.5°	81%	32

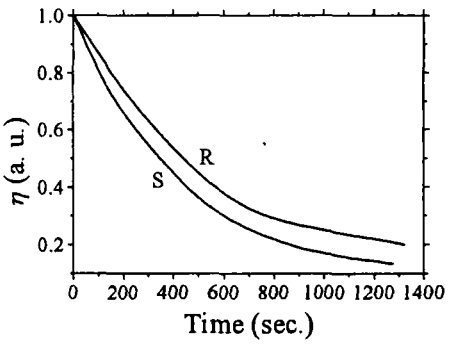

Figure 4. The erasure curve of the near-stoichiometric $LiNbO_3$.

Judgment of Styles of Light Excited Carrier [4]

When the electron was the main style of the light excited carrier in the erasure process, the erasure time of the signal light I_1 is shorter than that of the pump light. When the cavity was the main style of the light excited carrier in the erasure process, the erasure time of the signal light I_1 is longer than that of the pump light I_2. The erasure curves of near-stoichiometric Li were shown in Fig. 4. From Fig. 4, it could be seen that the erasure speed of the near-stoichiometric $LiNbO_3$ was faster than that of the congruent $LiNbO_3$. So the electron was the main style of the light excited carrier in the erasure process in near-stoichiometric $LiNbO_3$ crystal.

CONCLUSIONS

There are many intrinsic defects in the congruent $LiNbO_3$ crystal, the main styles of which are V_{Li+} and Nb_{Li}^{4+}. In the near-stoichiometric $LiNbO_3$, the defect number of V_{Li+} and Nb_{Li}^{4+} are significantly reduced. Compared with the congruent $LiNbO_3$, the ultraviolet-visible absorption edge of the near-stoichiometric $LiNbO_3$ shifted to ultraviolet band. The infrared absorption peak of the near-stoichiometric $LiNbO_3$ is shifted from 3483 cm^{-1} to 3466 cm^{-1}. The exponential gain coefficient of the near-stoichiometric $LiNbO_3$ was 24 cm^{-1}, which is 2.5 times higher than that of the congruent $LiNbO_3$. The diffraction efficiency of the near-stoichiometric $LiNbO_3$ achieved 42%. In Comparison with the congruent $LiNbO_3$, the response time of near-stoichiometric $LiNbO_3$ became shorter. The measurement results of the near-stoichiometric Fe:$LiNbO_3$ was that its Γ_{max} was 43 cm^{-1}, η_{max} was 70% and t was 5.6 seconds.

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