Femtosecond laser-induced sub-wavelength modification in lithium niobate single crystal

Benhai Yu¹,², Peixiang Lu¹,³, Nengli Dai¹, Yuhua Li¹, Xinlin Wang¹, Ying Wang¹ and Qiguang Zheng¹

¹ Wuhan National Laboratory for Optoelectronics Technology, Huazhong University of Science and Technology, 1037 Luoyu Road, Wuhan 430074, People’s Republic of China
² College of Physics and Electronics Engineering, Xinyang Normal University, Xinyang 464000, People’s Republic of China

E-mail: lupeixiang@mail.hust.edu.cn

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Abstract

The microstructural modification of lithium niobate (LiNbO₃) single crystal ablated by an 800 nm femtosecond laser pulse has been investigated. The ablation spots have been examined by means of scanning electron microscopy (SEM), atomic force microscopy (AFM) and Raman microscopy systems. Sub-wavelength spots in an LiNbO₃ crystal ablated by a femtosecond laser focused with a 20× microscope objective (NA = 0.5) have been achieved. The spot size is 400 and 800 nm with 170 nJ single-pulse and 100 nJ 17-pulse ablation, respectively. The periodic ripples on the bottom of the ablation spot were found, and it has a width of 100 nm and a period of roughly 200 nm between troughs. The results show that the sub-wavelength structures may be formed by the multiple-photon excitation, and the femtosecond laser ablation is an innovative tool for manufacturing LiNbO₃-based optical devices.

Keywords: femtosecond laser, lithium niobate, sub-wavelength

1. Introduction

Femtosecond laser-induced breakdown in transparent solid materials has been studied extensively and has received increased attention with the development of high-power femtosecond laser systems [1–5]. By tightly focusing a femtosecond laser beam into transparent materials, multiple-photon absorption produces highly localized plasma. The rapid expansion of the plasma causes a microexplosion. In this process, material is ejected from the center, forming a void surrounded by a region of compacted material. Void dots or void channels have been generated in a variety of materials such as silica glass [6], borosilicate glass [7, 8], phosphor glass [9], fluoride glass [10] and YAG [11]. This method has been used in fabricating waveguides [12], optics coupling devices [13] and three-dimensional (3D) optical storage devices in bulk transparent materials [14].

Lithium niobate single crystal is a well-known nonlinear crystal with a high refractive index of 2.2 and a wide transparent range of 0.5–5 μm. It is a key material for integrated optical devices used in widespread applications in nonlinear optics and telecommunications because of its large electro-optic and nonlinear coefficients and availability in high optical quality. Due to its excellent electro-optic properties, high-optical-quality single crystals of congruent and recently of stoichiometric composition are reproducibly grown for a range of applications in optical telecommunications for the fabrication of optical modulators, surface acoustic wave devices and nonlinear optics with periodically poled material. A femtosecond laser as a novel tool for material processing has been applied extensively. In recent years, some optical devices such as waveguides [15], gratings [16] fabricated in an LiNbO₃ single crystal by a femtosecond laser have been investigated, but little work has been done towards an extensive analysis of the microstructural modification. In this
Figure 1. CCD image of LiNbO$_3$ crystal after ablation with various energies of the femtosecond laser.

Figure 2. SEM images of LiNbO$_3$ crystal after ablation with single-pulse energies of the femtosecond laser: (a) 470 nJ, (b) 350 nJ, (c) 230 nJ, (d) 170 nJ.

Figure 3. The morphology and AFM image of LiNbO$_3$ after ablation with a 230 nJ single pulse.

paper, microstructural modifications of LiNbO$_3$ single crystals induced by a femtosecond laser pulse with a wavelength of 800 nm have been investigated. Sub-diffraction spots have been achieved and periodic ripples on the bottom surfaces of the spots ablated by multiple pulses at low laser energy have been observed.

2. Experiments

The experiments were performed using a commercial Ti:sapphire laser system (Spectra-Physics, USA), emitting linearly polarized light at a wavelength of 800 nm with a pulse duration of 50 fs and a pulse repetition rate of 1 kHz. The femtosecond laser pulse energy could change over the range of 0–2 mJ by using a polarization rotation attenuation filter. A fast acting shutter (0.001–1 s) controlled the number of laser pulses exposing the sample. The laser beam was focused by using a 20× (NA = 0.5) microscope objective and injected into the LiNbO$_3$ sample (10 × 5 × 0.5 mm, z-cut). The relation between the focus beam diameter $D$, the laser wavelength $\lambda$ and the numerical aperture NA is given as

$$D = 1.22 \times \frac{\lambda}{\text{NA}}$$

In our experiment, the focus beam diameter $D$ is about 2 $\mu$m. The sample could be controlled by moving the motorized stage (H101, Prior Inc. England) with a resolution of 0.03 $\mu$m (X, Y axes) and 1 $\mu$m (Z axis), respectively. Both the processing procedure and the status of modification could be observed via a Nikon charge coupled device (CCD) camera.

3. Results and discussions

3.1. Single-pulse ablation

The surface morphologies of the LiNbO$_3$ crystal produced by a single femtosecond pulse with various energies are shown in figure 1. The first row was ablated by a single pulse and the next seven rows by multiple pulses. All of the processing was performed in air under normal conditions of temperature and pressure.

The microstructural modifications of LiNbO$_3$ after ablation with a single pulse were observed with SEM and AFM as shown in figures 2 and 3, respectively. In our experiment, the single-pulse and 1000-pulse damage thresholds for LiNbO$_3$ are about 2.0 J cm$^{-2}$ and about 0.8 J cm$^{-2}$, respectively. It is observed that the damage threshold for 1000 pulses is far lower than that for single-pulse ablation. This effect could be attributed to defect-enhanced absorption. We can observe the microstructural variations in the LiNbO$_3$ crystal as the pulse energy is decreased from 470 to 170 nJ. The size of the ablation spot with 350 nJ single-pulse energy is similar to the wavelength (figure 2(b)), and the size of the ablation spot with 170 nJ single-pulse energy is about 400 nm, which is much smaller than the wavelength. No trace of surface structural change morphology is observed under CCD and SEM for the pulse energy less than 60 nJ. We can see that the morphology of the LiNbO$_3$ is quite different from that of glass induced by a femtosecond laser pulse [10, 11].

3.2. Multiple-pulse ablation

To obtain the damage threshold and microstructural modification for LiNbO$_3$ under the given processing parameters, seven
rows and ten vertical columns have been ablated using various pulse numbers and pulse energies (figure 4). Each of the vertical columns has been written using a different pulse number, so the pulse number of every ablation spot from column 1 to 10 is 2, 4, 8, 16, 31, 62, 125, 250, 500 and 1000, respectively. The pulse energy of every ablation spot from row 1 to 7 is 700, 470, 230, 180, 100, 60 and 50 nJ per pulse, respectively. We can observe the ablated area and depth are increased with increasing pulse energy and pulse number. The size of the ablation spot with few numbers or low energy of femtosecond pulses is smaller than the wavelength (figures 5(c)–(h)). The AFM image (figure 6) reveals the morphology ablated by 100 nJ, 17 pulses. The size is about 800 nm and the depth is about 320 nm, respectively. In addition, the clear edge, which is different from that ablated by a long pulse and may not be induced by thermal melting, was also observed. Many recent works \cite{17–20} have demonstrated that there are two major regimes of femtosecond pulse laser ablation: nonthermal ablation and thermal ablation. The ablation using low fluence and short pulse width is based on nonthermal ablation, and the long pulse width or high laser fluence is based on thermal ablation. The two ablation regimes are bordered by laser-fluence-dependent critical pulse widths. There is a transition between the two regimes influenced by laser fluence associated with the pulse width, and the higher the laser fluence, the shorter the critical pulse width. While the laser fluence is very high, the thermal ablation mechanism will be dominant and the heat effect will be evident \cite{21}. In our experiment, the laser fluences are near the damage threshold and the experimental results referred to nonthermal ablation.

In this experiment, there are periodic ripples on the bottom of the ablation spots at low laser energy or small number of laser shots. Laser-induced periodic surface structures (LIPSS), also termed ripples, were first observed by Birnbaum on some semiconductor surfaces \cite{22}. Since then, LIPSS have been reported on various materials. The LIPSS appear as the result of a nonlinear growth process which is initiated by the scattering of a small amount of light out of the primary laser beam by random irregularities initially present in or on the illuminated surface. These initial noise irregularities may be random variations in surface height, electron density, defect density or any other optically significant physical property \cite{23–26}. In our results, the ripples have a width of 100 nm and a period of roughly 200 nm between troughs (figures 5(c), (d), (g) and (h)). Because the period is less than the laser wavelength, we suggest that the formation of periodic nanostructure in our experiment should be related
Table 1. Vibration frequency and type of LiNbO₃ crystal for the unprocessed and processed points.

<table>
<thead>
<tr>
<th>Peak of point A (cm⁻¹)</th>
<th>Peak of point B (cm⁻¹)</th>
<th>Peak of point C (cm⁻¹)</th>
<th>Symmetry</th>
<th>Type of vibration</th>
</tr>
</thead>
<tbody>
<tr>
<td>152</td>
<td>152</td>
<td>151</td>
<td>E</td>
<td>Mutual nearly in-plane rocking of NbO₆ octahedron and nearly in-plane Li-vibration</td>
</tr>
<tr>
<td>238</td>
<td>238</td>
<td>238</td>
<td>E</td>
<td>Nb–O bond rocking, Nb–O–Nb bending or in-plane Li-vibration</td>
</tr>
<tr>
<td>262</td>
<td>263</td>
<td>259</td>
<td>E</td>
<td>In-plane Li-vibration, weak Nb–O bond rocking</td>
</tr>
<tr>
<td>321</td>
<td>320</td>
<td>320</td>
<td>E</td>
<td>O–Nb–O and O–Nb–O bending</td>
</tr>
<tr>
<td>330</td>
<td>330</td>
<td></td>
<td>E</td>
<td>O–Nb–O bending</td>
</tr>
<tr>
<td>366</td>
<td>366</td>
<td>367</td>
<td>E</td>
<td>O–Nb–O bending</td>
</tr>
<tr>
<td>431</td>
<td>431</td>
<td>429</td>
<td>E</td>
<td>O–Nb–O bending</td>
</tr>
<tr>
<td>580</td>
<td>580</td>
<td>580</td>
<td>E</td>
<td>Equatorial Nb–O stretch (doubly degenerate)</td>
</tr>
<tr>
<td>619</td>
<td></td>
<td>619</td>
<td>A₁</td>
<td>Nb–O stretch</td>
</tr>
<tr>
<td>738</td>
<td>738</td>
<td>736</td>
<td>A₁</td>
<td></td>
</tr>
<tr>
<td>880</td>
<td>881</td>
<td>885</td>
<td>A₁</td>
<td></td>
</tr>
</tbody>
</table>

Figure 7. (a) CCD image of LiNbO₃ after ablation by a femtosecond laser. (b) Raman spectra of the points indicated by the letters in (a).

3.3. Raman spectra analysis

The Raman spectra were measured with a laser confocal Raman microscope system of a 10 mW, 632.8 nm He–Ne laser, and recorded over a wavenumber range from 100 to 1000 cm⁻¹. The Raman spectra are measured at different points, from the processed region to the unprocessed region (figure 7). The irreducible representations for the space group R3c at the center Γ-point of the first Brillouin zone are 5A₁(Z) + 5A₂ + 10E(X, Y) [27]. For the point group 3m (C₃ᵥ), the Raman- and IR-active optical-phonon modes at the zero wavevector are 4A₁(Z) + 9E(X, Y). Depending on the scattering geometry, it is possible to have A₁ or E-type spectra. Due to the back-scattering geometry and the c-cut LiNbO₃, the resulting Raman spectra were mostly dominated by E-modes.

Among them the most intense is the Raman peak centered at about 880 cm⁻¹ [28].

In our experiment, the spectra of the unprocessed area (point A) and processed area (points B and C, the edge and the center of the processed area, respectively) were measured, and 10 peaks were observed. A description of the peaks is given in table 1. All the peaks in the unprocessed point A are observed in the processed point B, indicating that all of the elements present in the unprocessed sample are present in the processed sample. We can observe the intensity of the peaks for laser-processed LiNbO₃ is less than those for the unprocessed region. This indicates a constraint on the vibrational degrees of freedom of the molecule. This could be due to the introduction of defects and changes in physical structure. Comparing the spectra of points C and A, we can notice that the main peaks of point C are strongly reduced (peak at 330 cm⁻¹ has disappeared) and the peak at 619 cm⁻¹ increased markedly, thus indicating the presence of disordered crystal structure.

4. Conclusions

In summary, we characterized the microstructural modification of a lithium niobate crystal induced by femtosecond laser ablation using a CCD camera, SEM and AFM. Sub-wavelength spots in an LiNbO₃ crystal ablated by a femtosecond laser have been achieved. The spot size is 400 and 800 nm with 170 nJ single-pulse and 100 nJ, 17-pulse ablation, respectively. The sub-wavelength structures can be achieved by choosing the center intensity of the focused region slightly above the threshold value. In this case only the central part of the beam can ablate the material and it becomes possible to produce sub-wavelength structures. The periodic ripples on the bottom of the ablation spot were obtained. The ripples have a width of 100 nm and a period of roughly 200 nm between troughs. They are produced due to the interference of the incident laser with the scattered laser from a surface disturbance and the periodic structure of the crystal. Raman analysis indicates some loss of crystallinity of the material. This indicates that LiNbO₃ suffers some change in chemical structure at the superficial layer, but remains largely unchanged in the bulk.
Acknowledgments

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