Two-photon absorption in undoped LiTaO₃ crystals

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Article history:
Received 26 September 2017
Received in revised form 31 October 2017
Accepted 15 November 2017
Available online 22 February 2018

Abstract

The two-photon absorption (TPA) coefficient is obtained for pure lithium tantalate (LT) crystals as a function of \( C_L = 100\% \times \frac{Li_2O}{(Li_2O + Ta_2O_5)} \) ratio. Five LT samples with \( C_L = 47.95, 48.38, 48.75, 49.6 \) and 50 mol % were selected. The open Z-scan method was carried out to measure TPA coefficients at \( \lambda = 400 \) nm using 90 fs pulses at the appropriate pulse intensity of \( I_0 = 3.5 \text{–} 4 \text{ GW/cm}^2 \). The TPA coefficients in LT drastically increase with the Li content increase and they reach 3–4 cm/GW for the stoichiometric composition LiTaO₃. TPA exhibits its saturation behavior with the saturation intensity of 11 GW/cm².

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Keywords:
Two-photon absorption
Lithium tantalate
Composition
Z-scan method

1. Introduction

Two-photon absorption is among the key effects observed in high-power laser optics and it is of great importance when short (from nano- to femtosecond) light pulses interact with optical materials [1–6]. The TPA magnitude is a basic parameter of lightweight media and this parameter describes the intensity-dependent optical losses appeared on the light beam propagation [7–12]. In many aspects, this parameter defines the possible application fields of linear and nonlinear optical materials in pulse laser systems. Knowing the TPA coefficient value is important both in the case of two-photon multilayered information recording [8,13], when the losses connected with TPA are useful, and in the case of frequency conversion when the TPA effect is a destructive factor and limits the acceptable optical intensity level.

Lithium tantalate (LT) with stoichiometric composition LiTaO₃ crystallizes in polar noncentrosymmetric space group \( R3c \) (number 161) and, respectively, possesses a rich combination of ferroelectric, pyroelectric, nonlinear optical and piezoelectric properties [14–18]. The crystal structure of LT is shown in Fig. 1 [14,19]. \( Li^+ \) and \( Ta^{5+} \) ions are in the octahedral orientation. The LT structure can be considered as ordered stocks of face-shared octahedrons along polar direction [001], where each third octahedron in a column stock is empty. For the \( Li_2O-Ta_2O_5 \) binary system, it was found that the LT phase forms over a relatively wide range of ratio \( C_L = 100\% \times \frac{Li_2O}{(Li_2O + Ta_2O_5)} \) [20,21]. LT melts incongruously and the special methods are needed to reach the selected uniform composition over the large crystals grown by Czochralski technique [22,23]. Presently, the large-size, colorless, defect-free LT crystals are available for their optical and electronic application. However, it should be accounted that the physical properties of LT, including unit cell parameters, density, Curie temperature, refractive indices, acoustical and electrooptical constants, are dependent on the real crystal composition [20–29].

The present study is aimed at the determination of the LT crystal TPA coefficient and its dependence on the crystal composition. This is valuable for the LT application in holography, integrated optics and other optical systems [13,30–35]. It should be pointed that, for a correct determination of TPA coefficient, the femtosecond laser systems are preferable because, in this case, the influence of absorption processes from the excited state is minimal, as compared to that for nano- and picosecond laser pulses. Previously, the TPA coefficient (\( \beta \)) of the LT crystal was measured only in the LT-based waveguide layer at wavelength \( \lambda = 400 \) nm, and value \( \beta = 2 \text{ cm/GW} \) was reported on [36]. However, in this case, the waveguide was formed by the proton bombardment technique, when numerous structural defects generation is evident, and,
respectively, the measured value of $\beta$ can only be considered as an estimation \[30,32,37,38\]. Besides, dependence $\beta(C_{Li})$ remains unknown.

2. Samples

Five LT samples with lithium molar concentration $C_{Li} = 47.95$, 48.38, 48.75, 49.6 and 50 mol % were selected. The congruently melting LT has its lithium concentration of about 48.5 mol%. Therefore, the samples under research range from the so-called under congruent crystal (47.95 mol %) to the stoichiometric one (50 mol %). The crystals were grown by Czochralski method and, previously, they had been used in our several earlier experiments. The detailed information on the substrate parameters and the method of parameter $C_{Li}$ determination can be found elsewhere \[5,13,24\]. The absorption spectra of these crystals are shown in Fig. 2. The lithium concentration increase leads to the UV absorption edge shift to shorter wavelengths and, hence, to the increase of band-gap energy. Only the sample with $C_{Li} = 48.38$ mol % falls out from this well known regularity. According to \[39\], the absorption coefficients for ordinarily polarized light at 400 nm and 310 nm yield concentrations $C_{Fe^{2+}}$ and $C_{Fe^{3+}}$, respectively. The iron concentrations obtained by this method are summarized in Table 1. If we assume that iron is the most common uncontrollable impurity, the samples can be considered as conventionally undoped because, as one can see in Table 1, its concentration $C_{Fe}$ is below $10^{16}$ cm$^{-3}$ in all the samples. However, one can see from the data in Table 1, the sample with $C_{Li} = 48.38$ mol % contains the highest concentration of Fe$^{3+}$ centers. This factor can induce an additional shoulder in the absorption spectrum near the wavelength of 310 nm and, respectively, it can provide a long-wave shift of the absorption edge for the sample.

3. Experimental methods

A sensitive and experimentally simple open Z-scan method was used to measure TPA coefficients. We applied a new approach to the analysis of open Z-scan experiments \[40\], which permits to account for the Gaussian beam ellipticity and astigmatism. The TPA coefficient was measured using the optical setup shown in Fig. 3. Femtopower compact Pro (Femtolasers) laser system (1) was used to generate 30 fs pulses with a pulse energy ~ 0.6 mJ centered at 800 nm at the repetition rate of 100 Hz. The reflecting telescope (3) was applied to decrease the laser beam diameter from 16 to 2 mm. Frequency doubling was carried out in the nonlinear BBO crystal with the thickness of 0.3 mm (4). To control the laser pulse width, the radiation at the fundamental frequency and the second harmonic radiation were transferred to the input of the SPIDER SP-0.8-2f (2) system used for the magnitude and phase characteristics analysis of the femtosecond laser pulse. The second harmonic pulse width $(\lambda = 400 \text{ nm})$ was 60 fs (FWHM). Furthermore, since the blue pulses traveled through the focusing lens (5), they prolonged in time. We estimate the pulse width at the crystal face to be nearly 90 fs (FWHM). The use of such short pulses permits minimizing the influence of the absorption from excited states. The spatial and temporal distribution of the pulses was nearly Gaussian. The samples under investigation (6) were installed on the two-dimensional positioner. The pass beam energy was monitored by the measuring head PD10 Ophir (7) created on the base of Si photodiode. The input energy was recorded by the OPHIR II (8) meter. The results were processed by a computer (9).

4. Results and discussion

The TPA coefficients of undoped LT crystals were measured by the Z-scan method with an open aperture using 90 fs laser pulses. The laser beam was focused by the lens with the focal length of 100 mm, producing the beam waist of 12 $\mu$m. The corresponding diffraction length inside the LT crystal with refractive index $n = 2.3$ was $z_{Diff} = 2.6$ mm (where $z_R$ is the Rayleigh length), which significantly exceeds the samples thickness of 0.5–1 mm. The measurements were carried out for several incident beam intensity values, lying in the range of 3–50 GW/cm$^2$. LT crystals are characterized by high optical damage thresholds and, respectively, optical damage effects were not detected in our experiment. The input lightwave polarization was parallel to the optical axis of the crystal. The TPA coefficient values obtained as a function of input pulse

### Table 1

Concentration of iron, as determined by absorption spectra analysis \[39\].

<table>
<thead>
<tr>
<th>$C_{Fe}$ (mol %)</th>
<th>$C_{Fe^{2+}}$ (x 10$^{17}$ cm$^{-3}$)</th>
<th>$C_{Fe^{3+}}$ (x 10$^{17}$ cm$^{-3}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>47.95</td>
<td>1.43</td>
<td>5.12</td>
</tr>
<tr>
<td>48.38</td>
<td>1.96</td>
<td>6.55</td>
</tr>
<tr>
<td>48.75</td>
<td>2.13</td>
<td>11.61</td>
</tr>
<tr>
<td>49.6</td>
<td>0.36</td>
<td>4.48</td>
</tr>
<tr>
<td>50</td>
<td>1.38</td>
<td>4.52</td>
</tr>
</tbody>
</table>

Fig. 1. The fragment of LiTaO$_3$ crystal structure. The unit cell is outlined. Lone atoms are omitted for clarity.

Fig. 2. Absorption spectra of LT crystals with different $C_{Li}$. All measurements of TPA coefficients were carried out at the wavelength of $\lambda = 400$ nm.
intensity for three LT crystals different in their composition are shown in Fig. 4. The TPA coefficient determination precision was as low as ±15%. It is clear that, for all the samples, the TPA coefficient decreases with the input pulse intensity increase. Generally, the TPA coefficient can be affected by the light absorption by electrons at upper excited levels and by the TPA saturation. However, the light absorption at excited states can only increase the absorption coefficient. Thus, it can be assumed that the TPA decrease is induced by the saturation effect.

To test this supposition, the one-beam transmission measurements without Z-scanning were made. In the experiments, the thin long-focus lens (6) was used to minimize the pulse width increase. The pulse width was estimated to be 61 fs (FWHM) and the beam width in the focus was \( u_0 = 50 \) μm. The results of this experiment are shown in Fig. 5 (filled rhombs), where the reciprocal energy transmission is plotted versus the maximum on-axis intensity. It is evident that the optical transmission drastically decreases at higher pulse intensities. A simple model is proposed to describe the pulse intensity variation on the propagation in the nonlinear medium. In this model, the intensity variation can be expressed with the relation:

\[
dI = -\beta(I)I^2dz.
\]  

(1)

A hyperbolic approximation is used to model the intensity dependence of TPA coefficient \( \beta \)

\[
\beta(I) = \beta_0/(1 + I/I_{sat})
\]  

(2)

where \( \beta_0 \) is the TPA coefficient at low pulse intensity, \( I_{sat} \) is the pulse intensity which induces the two-fold TPA coefficient decrease. The similar TPA dependence was earlier found in several semiconductor materials, for example in CdS [41].

By the substitution of (2) to (1), accounting that input and output external intensities \( (I_{in}, I_{out}) \) are related to internal input and output intensities \( (I_{in}', I_{out}') \) by equations \( I_{in} = I_{in}'/(1 - R) \) and \( I_{out} = I_{out}'(1 - R) \), where \( R \) is the reflection coefficient, the analytical solution can be found for equation (1) [41]:

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Fig. 3. Optical scheme of the experimental setup for the femtosecond measurements of two-photon absorption coefficient.

Fig. 4. Dependence of TPA coefficient measured by the open-aperture Z-scan technique on incident intensity \( I_0 \) for LT crystals with different \( C_{Li} \). The solid lines are the fits using hyperbolic functions.

Fig. 5. Nonlinear energy transmission and numerical modeling for the LT crystal with \( C_{Li} = 49.6 \) mol%. The filled rhombs are plots of the measured reciprocal energy transmittance \( (1/T) \) versus incident intensity \( (I_0) \). The solid line is the theoretical fitting with the use of the TPA saturation model, where \( \beta_0 = 5.1 \) cm/GW, \( I_{sat} = 11 \) GW/cm². The dotted line is a theoretical curve calculated for the unsaturated TPA coefficient \( (\beta_0 = 5.1 \) cm/GW).
where \( d \) is a sample thickness. The transmitted intensity was numerically calculated and, then, it was spatially and temporally integrated to get the transmitted energy, because just the energy was measured experimentally. The \( \beta_0 \) value was determined by the Z-scan method at a low intensity (see Fig. 4), where the TPA saturation is negligible. For the crystal with the Z-scan method at a low intensity (see Fig. 4), where the TPA in Fig. 5. Thus, it can be concluded that the experimental data curve calculated without accounting the TPA saturation is shown in Fig. 5. Thus, it can be concluded that the experimental data shown in Fig. 5 can be well described by the model accounting the TPA saturation at high pulse intensities. At the pulse width of 61 fs and the wavelength of 400 nm, the saturation intensity is 11 GW/cm².

The final measurements of TPA coefficients \( \beta_0 \) were carried out at the appropriate pulse intensity of \( I_0 = 3.5–4 \) GW/cm², when the saturation effects can be neglected. The results obtained for LT crystals with different \( C_{Li} \) are shown in Fig. 6. One can see from the data in Fig. 6 that, for both light polarization, the TPA coefficients in LT drastically increase with the Li content increase and they reach 3–4 cm/GW for the stoichiometric composition LiTaO₃. This trend is in contrast to the “two-band” model commonly applied to the oxide crystals [42]. According to the model, the TPA coefficient should be lower in the crystals with a higher band gap (higher \( C_{Li} \) in LT). The reason for the opposite effect in LT is currently unclear. However, it may be assumed that the “two-band” model is not precise in the LT-type materials.

It is supposed that the TPA coefficient in oxide crystals is governed by electron transitions from the valence band to conduction band. At the same time, the two photon absorption related to electron transitions from the valence band to the Fe³⁺ and Ta⁵⁺ states can not be neglected. However, the transitions cannot be dominant because the number of the Fe³⁺ and Ta⁵⁺ states is evidently lower than the number of valence band states. Earlier, for the LiNbO₃ (LN) crystals, the dependence of the TPA coefficient on the doping level was evaluated in several studies [43,44]. Generally, a very low sensitivity of TPA coefficient to the impurity level was found. This indicates that the major effect comes from the crystal matrix. Accounting the known LN and LT isomorphism, the same relation can be reasonably assumed in LT.

Besides, it is interesting to compare the two-photon absorption level in LT with those known for commonly used optical materials. A collection of the parameters earlier reported on for representative linear and nonlinear optical crystals is shown in Table 2. As it is seen from Table 2, the isomorphous LT and LN crystals possess comparatively high two-photon absorption coefficients, and this factor should result in a significant decrease of the high-power light beams in these crystals. Besides, the specific feature of LT and LN is the permanent changes of the refractive index caused by the two-photon-induced photorefraction [13]. Due to this effect, for example, the Gauss-profile light beam can generate lens-like features and that results in an additional light scattering. It should be pointed, however, that, at light intensities above the saturation value (11 GW/cm² for stoichiometric LT), the two-photon absorption effect decreases.

5. Conclusions

As it is elucidated in the present study, the two-photon absorption in LT is comparatively high and the level is strongly dependent on the \( C_{Li} = 100\% \times Li_2O/(Li_2O + Ta_2O_5) \) ratio. In this experiment, to minimize the influence of absorption processes from the excited state, the measurements were carried out by the fs

![Fig. 6. Composition dependence of TPA coefficient \( \beta \). The laser pulse polarization vector is parallel to the \( c \) axis (filled rhombs) or perpendicular to the \( c \) axis (filled triangles). The dotted lines are visual/eye guides.](image)

### Table 2

<table>
<thead>
<tr>
<th>Crystal</th>
<th>Length, nm</th>
<th>( \lambda ) nm</th>
<th>( \tau ) fs</th>
<th>( \varepsilon ) cm⁻¹</th>
<th>( \beta ) cm/GW</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>CdS</td>
<td>0.13</td>
<td>630</td>
<td>100 fs</td>
<td>2.7</td>
<td></td>
<td>[41]</td>
</tr>
<tr>
<td>GaSe</td>
<td>7.5</td>
<td>700</td>
<td>200 fs</td>
<td>2.16</td>
<td></td>
<td>[45]</td>
</tr>
<tr>
<td>CsPbBr₃</td>
<td>194 nm</td>
<td>800</td>
<td>80 fs</td>
<td>4.73</td>
<td></td>
<td>[46]</td>
</tr>
<tr>
<td>KI₃PO₄ (KDP)</td>
<td>15</td>
<td>248</td>
<td>650 fs</td>
<td>0.05</td>
<td>0.48</td>
<td>[47]</td>
</tr>
<tr>
<td>KI₃Ba₂O₄ (BBO)</td>
<td>5</td>
<td>248</td>
<td>650 fs</td>
<td>0.01</td>
<td>0.02</td>
<td>[47]</td>
</tr>
<tr>
<td>Cs₂LiBO₃</td>
<td>14</td>
<td>248</td>
<td>650 fs</td>
<td>0.02</td>
<td>0.53</td>
<td>[47]</td>
</tr>
<tr>
<td>Fused silica</td>
<td>9</td>
<td>264</td>
<td>200 fs</td>
<td>0.019–0.024</td>
<td></td>
<td>[48]</td>
</tr>
<tr>
<td>Crystaline quartz</td>
<td>1.38</td>
<td>264</td>
<td>200 fs</td>
<td>0.0129</td>
<td></td>
<td>[48]</td>
</tr>
<tr>
<td>Al₂O₃ (sapphire)</td>
<td>0.6</td>
<td>264</td>
<td>200 fs</td>
<td>0.0940</td>
<td></td>
<td>[48]</td>
</tr>
<tr>
<td>ZrO</td>
<td>500–700</td>
<td>150 fs</td>
<td>0.1–1</td>
<td>1.5</td>
<td></td>
<td>[49]</td>
</tr>
<tr>
<td>TiO₂ (rutile)</td>
<td>1</td>
<td>800</td>
<td>50 fs</td>
<td>1.5</td>
<td></td>
<td>[50]</td>
</tr>
<tr>
<td>Diamond</td>
<td>0.25</td>
<td>310</td>
<td>135 fs</td>
<td>0.75</td>
<td></td>
<td>[51]</td>
</tr>
<tr>
<td>LiNbO₃ (nanocrystals)</td>
<td>560</td>
<td>120 fs</td>
<td>–</td>
<td>1.3</td>
<td></td>
<td>[52]</td>
</tr>
<tr>
<td>LiNbO₃ (0.07–1)</td>
<td>388</td>
<td>240 fs</td>
<td>–</td>
<td>3.5</td>
<td></td>
<td>[53]</td>
</tr>
<tr>
<td>(H, Li)TaO₃</td>
<td>7</td>
<td>400</td>
<td>100 fs</td>
<td>2</td>
<td>0.1</td>
<td>[36]</td>
</tr>
<tr>
<td>LiTaO₃</td>
<td>0.5–1</td>
<td>400</td>
<td>61 fs</td>
<td>0.02–1</td>
<td>1–4</td>
<td>This study</td>
</tr>
</tbody>
</table>
pulse technique. The interband TPA saturation was observed in the LT crystal with the saturation intensity of 11 GW/cm². Thus, it can be concluded that, for the use in high-power laser systems, the LT crystals should be grown with the precise Li/Nb ratio control over the crystal bulk.

The mechanism of TPA increase with the Li content increase in LT is unclear for us. The role of Fe impurities seems to be only of a secondary level. As the reasonable next step after the present study, the observation of the TPA coefficient in the LN crystals with different Li/Nb ratio is topical. The LN and LT crystals are isomorphic and, respectively, many physical properties are similar in the materials. Then, the creation of a developed model of the TPA effect in the crystal family could be performed.

Acknowledgements

The reported study was funded by RFBR according to research projects 16-52-40108 and 17-52-53031.

References


