Optical Studies of Laser-Induced Gray-Tracking in KTP

B. Boulanger, I. Rousseau, J. P. Fève, M. Maglione, B. Ménéaert, and G. Marnier

Abstract—We have studied gray-tracking induced by a pulsed and polarized 532-nm laser beam in flux grown KTiOPO₄ (KTP) crystals. Transmission spectra measured under polarized light give different results: gray-tracking leads to an increase in the initial anisotropy of the linear optical properties of KTP, and the polar axis is the most sensitive to this process. The dynamics of relaxation of gray-tracking is anisotropic and depends on the wavelength under analysis. We show a possible induced modification of the crystal surface and also the existence of an intensity above which gray-tracking reaches the saturation point. We then measure the temperature above which gray-tracking no longer exists.

Index Terms—Anisotropic media, nonlinear media, photochromism, potassium compounds, titanium compounds.

I. INTRODUCTION

LASER-INDUCED damage in KTP, termed gray-tracking, is a detrimental effect which is observed during 1064-nm second-harmonic generation (SHG) [1]–[4] and optical parametric oscillation (OPO) pumped at 532 nm [5].

Gray-tracking induced by a laser is classically studied on the basis of several types of experiments: visual observation of the darkening, observation of second-harmonic beam distortion during 1064-nm SHG [3], [4], optical transmission coefficient measurement by the beam which creates the damage [6] or by a probe beam during laser exposure [1], [2], [7], optical transmission or absorption spectra [2], [8]–[11], and electron-spin-resonance (ESR) spectra [6], [8] measured before and after laser irradiation. From these experiments, some properties of the laser-induced gray-tracking have been determined: damage leads to a decrease in optical transmission over the entire visible range from 400 to 700 nm [2], [9], [11] with a magnitude which is a nonlinear function of the intensity of the laser beam creating the damage [2], [12]; the gray-tracking threshold, expressed as the laser peak intensity above which the damage is observed, is a decreasing exponential function of the Q-switch frequency [4]; a laser beam with a polarization parallel to the polar axis of KTP, i.e., the binary axis (z), creates more damage than a beam polarized orthogonally to the z axis [6], [9]; the time constant, usually a few minutes at room temperature, is dependent on the intensity of the laser beam until the level of gray-tracking reaches the asymptotic value [6], [7], [10], [12]. After the termination of laser exposure, the relaxation of the damage depends on the focusing conditions of the exposure beam, usually more than one year for strong focusing [4] and few hours for weak focusing [12] at room temperature. In all cases, the recovery time is much longer than that required to create the gray-track. Furthermore, the transmission recovery time decreases by heating the crystal [1], [2], [11], [13], and the gray-track does not form at high temperatures between 100 °C and 150 °C [3], [11]. The susceptibility to gray-tracking depends on the crystal growth conditions, either for the hydrothermal method or the flux method [9], [14], but it is difficult to make a correlation with the initial crystal defectiveness, i.e., the nature and concentration of the impurities and vacancies. A possible mechanism is based on the trapping of holes by Fe³⁺ ions and electrons by Ti⁴⁺ ions which are adjacent to an oxygen vacancy [15].

This research provides a comprehensive study of the anisotropy of the properties of laser-induced gray-tracking: the influence of the polarization of the beam which creates the damage, induced absorption, induced variation of Fresnel transmission, and the dynamics of relaxation. We also study the influences of the laser beam intensity and of the crystal temperature on the gray-tracking level. These experiments are performed on several uncoated KTP crystals which are grown by the top-seeded solution growth method (TSSG) from K₃PO₄O₁₃ [16], [17] and KPO₃–KF [18] fluxes: all the crystals under study show the same gray-tracking susceptibility to within the accuracy of our optical transmission measurements. The damage is induced by a 10-Hz Q-switch laser beam at 532 nm.

II. ANISOTROPIES OF CREATION AND RELAXATION OF THE GRAY-TRACK

A. Creation

In most previous research, the optical transmission spectra of laser-induced gray-tracking were measured under unpolarized light. Polarized light spectra have only been observed twice. The first time, KTP was modified by an exposure to 1 atm of H₂ followed by annealing at 650 °C in air or by a 200-µA-cm⁻² applied current along the z axis [19]; the second time, the gray-track was created by annealing in a vacuum at 670 °C or by X-ray irradiation at 15 K [20].

In this research, the spectra are obtained from 300 to 3000 nm with an accuracy of about ±0.5% using a spectrophotometer (VARIAN-CARY 5E) which we modified for...
crystal measurements with polarized light. We studied 2.7-, 5.0-, and 8.0-mm-thick KTP crystals cut at \( \theta = 90^\circ \) and \( \phi = 23.3^\circ \), which are the spherical coordinates of type II 1064-nm SHG phase-matching direction in the \( xy \) plane. The 532-nm beam is emitted by a seeded \( Q \)-switched and frequency-doubled Nd:YAG laser (BMI-5021 DNS) having the following characteristics: TEM\textsubscript{00}, single longitudinal mode, 10 Hz and 6.5-ns half-width duration at 1/\( e^2 \). A telescope reduces the beam radius to 1.2 mm (1/\( e^2 \)) inside the crystal. Each transmission spectrum is measured before and after the laser exposure of 25 min, which is longer than the time required for gray-tracking to reach the saturation point. All the experiments are performed with a 532-nm peak intensity of 155 MW/cm\(^2\) at the entrance of the crystal, and, under these conditions, the damage reaches an asymptotic level after being exposed for about 15 min. The optical transmission spectra of each crystal are measured parallel and orthogonal to the \( z \) axis, first before irradiation (\( \tau_{NIR} \) and \( \tau_{xy}^{NIR} \), respectively), and then after laser irradiation with a polarization parallel and orthogonal to the \( z \) axis (\( \tau_{HZ} \), \( \tau_{xy} \), \( \tau_{Z} \), and \( \tau_{xy}^{IR} \), respectively), where \( NIR \) and \( IR \) signify nonirradiated and irradiated, respectively. Between the two experiments, the crystal is heated for two days at 100 \( ^\circ \)C, which is the condition for KTP to recover completely from gray-tracking, according to our measurements. Furthermore, the spectra are taken in the first 10 min immediately after irradiation, which is quick compared with the recovery time.

In Fig. 1, we show an example of measurements over the visible range which are performed with the 8-mm-thick KTP crystal. The difference between the nonirradiated and irradiated crystal spectra, \( \tau_{HZ} - \tau_{xy}^{NIR} \), is plotted in order to individualize the gray-tracking signature. All the spectra have the same ultraviolet (UV) band-edge wavelength of 350 nm. For all the configurations of polarization, the visible range is modified by the damage: two bands can be indentified, around 390 and 500 nm. The band which peaks at 390 nm is possibly due to either Fe\textsuperscript{3+} or Fe\textsuperscript{4+} ions while the band peaking at 500 nm is attributed to Ti\textsuperscript{3+} ions [8], [15], [20]. The spectra which we obtain have the same behavior as a spectrum obtained with unpolarized light after gray-tracking during 1064-nm SHG [2], [8]. This is not surprising because it has been demonstrated that the damage is only caused by the generated second-harmonic beam, at 532 nm, with the fundamental beam having no influence [12].

For each polarization of analysis, the gray-tracking intensity depends on the polarization of the beam which creates the damage, i.e., \( \tau_{HZ} - \tau_{xy}^{NIR} \) over the entire visible range. The gray-tracking susceptibility is greater when the 532-nm beam polarization is parallel to the \( z \) axis. This result corroborates previous measurements performed with a probe beam at 532 nm [6] and with white light [9]. Furthermore, our work indicates that this effect is higher for \( Tz \) than for \( Txy \).

From these experiments, we also demonstrate that the laser-induced gray-tracking increases the initial anisotropy, expressed as \( \tau_{xy}/\tau_{xy}^{NIR} \), as shown in Fig. 2. This effect is weak when the 532-nm beam polarization is orthogonal to the \( z \) axis, but it is particularly important for a \( z \)-polarized beam.

In all previously published research, the absorption coefficient is obtained from the transmission coefficient on the assumption that Fresnel transmission is not modified by the damage. Here we separate the surface and volume contributions of the transmission by fitting the transmission spectra of the 2.7-, 5.0-, and 8-mm-thick KTP crystals using the Beer–Lambert equation

\[
\ln \tau(\lambda, L) = 2 \ln T(\lambda) - \alpha(\lambda)L
\]

where \( T(\lambda) \) is the Fresnel transmission (at wavelength \( \lambda \)) of one surface, \( \alpha(\lambda) \) is the single photon absorption coefficient, and \( L \) is the crystal length. The examples given in Table I are the numerical values which correspond to 390 and 500 nm. It seems clear that the induced absorption parallel to the \( z \) axis, \( \alpha_{52} \), is maximum when the polarization of the...
TABLE I

<table>
<thead>
<tr>
<th></th>
<th>( \alpha_Z ) (% cm(^{-1}))</th>
<th>( \alpha_{XY} ) (% cm(^{-1}))</th>
<th>( T_Z ) (%)</th>
<th>( T_{XY} ) (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \lambda = )</td>
<td>390 nm</td>
<td>500 nm</td>
<td>390 nm</td>
<td>500 nm</td>
</tr>
<tr>
<td>Before damage (Calculated)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Before damage (Measured)</td>
<td>19.3 ± 1.7</td>
<td>3.3 ± 1.2</td>
<td>10.38 ± 0.15</td>
<td>2.99 ± 0.74</td>
</tr>
<tr>
<td>After damage ( I_{Z,532} ) (Measured)</td>
<td>33.4 ± 4.5</td>
<td>9.6 ± 0.5</td>
<td>13.8 ± 4.5</td>
<td>4.46 ± 1.71</td>
</tr>
<tr>
<td>After damage ( I_{XY,532} ) (Measured)</td>
<td>26.06 ± 0.85</td>
<td>6.21 ± 0.03</td>
<td>15.6 ± 0.7</td>
<td>4.42 ± 0.03</td>
</tr>
</tbody>
</table>

Fig. 2. Transmission anisotropy \( \tau_z/\tau_{XY} \) before and after 532-nm laser irradiation at 155 MW/cm\(^2\), \( I_{Z,532} \) 532 nm and \( I_{XY,532} \) 532 nm denote, respectively, irradiation polarized parallel and orthogonal to the \( z \) axis. \( L \) is the thickness of the crystal along the beam propagation direction with spherical coordinates \((\theta, \phi)\) and \( S \) is the cross section of the crystal.

Our measurements are not accurate enough to see this effect for \( \alpha_{xy} \). In any case, the absorption coefficients which we determined for the nonirradiated crystals have magnitudes typical of flux grown KTP. Our measurements indicate a significant decrease in the Fresnel transmission due to gray-tracking despite the inaccuracy of our method for that kind of measurement. Nevertheless, this decrease appears with the same magnitude for every wavelength in the visible range. This shift has to be interpreted carefully. Indeed, if we take the simplest expression of the Fresnel transmission, i.e.,

\[
T = 1 - (n - 1/n + 1)^2,
\]

the refractive index modification which corresponds to the observed variation of transmission is very strong: for \( n_z \), for example, the variation is about 0.02 or 0.05 for a beam polarization parallel or perpendicular to the \( z \) axis, respectively. We cannot estimate the variation of birefringence \( n_z - n_{xy} \) from our measurements because of the inaccuracies, but it is probably quite high. In this hypothesis, such variations in the bulk would dramatically change the phase-matching properties, which were never observed. The optimization of the SHG conversion efficiency during gray-tracking does not require an angular correction greater than 1° or 2° which correspond to refractive index variations of about \( 10^{-4} \) to \( 10^{-5} \). These variations are probably essentially due to the photorefractive effect [3] or to a change in temperature related to the increase in the absorption coefficient [21]. Therefore, if the Fresnel transmission variation which we observed is not an artifact, it is necessary to interpret it by a phenomenon located at the two interfaces of the crystal which are in contact with the laser beam. A good way to verify this hypothesis would be to perform ellipsometric measurements.

**B. Relaxation**

We study the dynamics of relaxation with a 10.39-mm-thick KTP crystal cut at \( \theta = 90^\circ \), \( \phi = 90^\circ \) (\( y \) axis). The crystal is gray-tracked above its saturation intensity with the 532-nm beam polarized orthogonal to the \( z \) axis. The two transmission spectra, with polarization parallel \( (\tau_{Z}^{IR}) \) and perpendicular \( (\tau_{XY}^{IR}) \) to the \( z \) axis, are recorded for 48 h after irradiation. The crystal is heated at 180 °C for 4 h between the two experiments. The time evolution of \( \tau_{Z}^{IR}/\tau_{XY}^{IR} \) is given in Fig. 3(a) for three wavelengths in the visible range.

The initial relaxation, which lasted about 13 h, is fitted using an exponential equation for each wavelength

\[
\tau^{IR}(\lambda, \tau) = \tau^\infty(\lambda) - [\tau^\infty(\lambda) - \tau_0^{IR}(\lambda)] \exp \left( -\frac{t}{t_0(\lambda)} \right)
\]

where \( \tau^\infty(\lambda) \) is the asymptotical transmission and \( \tau_0^{IR}(\lambda) \) is the transmission immediately after irradiation. Fig. 3(a) shows
Fig. 3. (a) Time relaxation of \(\tau_{IRX}/\tau_{NIR}\) for several wavelengths under analysis \(\lambda\). The continuous lines are fit using an exponential relaxation starting immediately after irradiation for about 800 min. The dashed lines are guides for the eyes. (b) Exponential relaxation time versus wavelength deduced from fitting \(\tau_{IRX}/\tau_{NIR}\) relaxation curves. (c) Wavelength dependence of the initial recovery rate deduced from fitting \(\tau_{IRX}/\tau_{NIR}\) relaxation curves. For all three figures, \(L\) is the thickness of the crystal along the beam propagation direction with spherical coordinates \((\theta, \phi)\) and \(S\) is the cross section of the crystal.

III. INFLUENCE OF THE LASER BEAM INTENSITY AND SATURATION EFFECT

The 532-nm laser beam intensity dependence of gray-tracking is studied by probing a 10-mm-thick KTP crystal cut at \(\theta = 90^\circ\) and \(\phi = 23.5^\circ\) at a fixed wavelength. A CW He–Ne laser at 632.8 nm is split into two beams: the probe and reference beams. The probe and 532-nm beams are coaxial and have the same diameter and polarization, parallel to the \(z\) axis of KTP. The reference does not propagate through the crystal. The probe and reference powers are measured with silicon photodiodes connected to lock-in amplifiers. The ratio between the probe power at the exit of the crystal and the reference power is measured before and after irradiation for different values of intensity of the 532-nm beam up to 200
MW/cm$^2$. The 532-nm beam maintains a constant diameter, the same as before, and the variation of intensity is obtained by increasing the pulse energy. The crystal is heated at 180 °C for 4 h to regain initial transparency between the two irradiations. We give in Fig. 4 the ratio $\tau_{ierz}/\tau_{ier}$, as a function of the 532-nm beam intensity. The transmission signal is taken at its asymptotic value—that is to say, after an irradiation of 15 min.

The curve in Fig. 4 shows undoubtedly that gray-tracking reaches an asymptotic level at about 100 MW/cm$^2$. Above this intensity, $\tau_{ierz}/\tau_{ier}$ remains equal to 96%. This result is very important because it states that a saturation point of gray-tracking can be reached: it corresponds to the maximum concentration of color centers which can be created in a given KTP crystal. The concentration of color centers corresponding to the saturation could then be calculated by knowing the number of photons involved in one elementary process and the quantum efficiency of this process. We only know that gray-tracking is based on a nonlinear absorption process, as is shown by the decreasing part of the curve in Fig. 4 and as it has been demonstrated in previous research [12]. Nevertheless, it is interesting to perform the calculation by making simplifying hypotheses: if one type of color center is created by a two-photon process with a quantum efficiency of 1, the total number of photons which have irradiated the crystal during 15 min of exposure, about 2.4-10$^{20}$, leads to a color center concentration of about 2.4-10$^{21}$ cm$^{-3}$, according to the beam geometry. With this hypothesis, one fourth of the molecules of KTP are associated with a color center according to the geometry. With this hypothesis, one fourth of the molecules of KTP are associated with a color center according to the geometry.

IV. INFLUENCE OF CRYSTAL TEMPERATURE AND GRAY-TRACKING VANISHING

The temperature dependence of gray-tracking is studied with a 10-mm-thick KTP crystal with the experimental setup used for the above measurement of the saturation intensity. The crystal is heated from room temperature to 170 °C during a 532-nm beam exposure at 145 MW/cm$^2$. Between the two experiments corresponding to two different temperatures, the crystal is heated at 180 °C for 4 h. The curves in Fig. 5 give the ratio $\tau_{ierz}/\tau_{ier}$ as a function of temperature. It shows that gray-tracking decreases as the temperature increases: the damage does not form at 170 °C. This temperature is higher than that measured in previous research where the gray-tracking levels are different: 75 °C [1], 65 °C [2], 150 °C [3], and in the range 100 °C–150 °C [11].

V. CONCLUSION

We have done a comprehensive and quantitative study of anisotropy of the optical properties of laser-induced gray-tracking where we demonstrated that damage leads to an increase in the initial transmission anisotropy and that the
relaxation rate is the quickest along the polar axis. We have also shown that the dynamics of relaxation depend on the wavelength of analysis and that there exists an intensity saturation effect corresponding to the maximum number of color centers which can be created in a given crystal. Furthermore, we considered a possible induced modification of the crystal surface.

ACKNOWLEDGMENT

The KTP crystals were provided by Crystal Laser SA.

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