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Femtosecond laser writing in the monoclinic $RbPb_2Cl_5:Dy^{3+}$ crystal

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ABSTRACT

Monoclinic $RbPb_2Cl_5$:Dy single crystal was tested for femtosecond laser writing at wavelength of 800 nm. Dependence of permanent refractive index change upon input pulse energy was investigated. Non-linear coefficients of multiphoton absorption and self-focusing were measured. Kerr non-linear coefficient was found to be as high as $4.0 * 10^{-6}$ cm^2/GW.

1. Introduction

Recent advances in non-linear mid-IR photonics are predominantly due to progress in technology of low loss materials and development of waveguide manufacturing [1,2]. The femtosecond laser writing is an effective and flexible tool for waveguide fabrication, but only few works were done in the field of femtosecond waveguide writing in mid-IR materials and almost all of them are devoted to zinc chalcogenide crystals [3,4]. Investigation of other mid-IR crystal and glasses is highly desirable for progress of waveguide writing for applications in mid-IR.

The $RbPb_2Cl_5$ (RPC) crystal has wide transparency window ranging from 0.3 μm to 20 μm. Energy of the most energetic phonon in this crystal is as low as 203 cm^{-1} [5]. These circumstances make this crystal to be very attractive for mid-IR application as a laser host material. Oscillation based on electronic transitions in Pr^{3+} and Dy^{3+} doped ions has already demonstrated in mid-IR [6,7]. However low segregation coefficient of rare-earth ions makes problematic efficient pumping of bulk laser elements. Waveguide architecture of laser could resolve the problem, because it allows keep high intensity of pumping on longer optical path than a scheme with free space pumping beam.

Successful implementation of femtosecond writing technique requires knowledge of non-linear optical properties of a material. In our previous study we have estimated that femtosecond inscription threshold is comparatively low in this crystal [8]. Other non-linear properties are not investigated yet. In this paper we present results on experimental investigation of multiphoton absorption (MPA), Kerr nonlinearity and permanent modification of refractive index under exposure of femtosecond pulses.

2. Sample

The RPC crystal is biaxial and belongs to the monoclinic crystal class, symmetry space-group is $P2_1/c$. Details of crystal structure could be found in [9]. The optical indicatrix is expected to be anisotropic for this crystal, like for KPb_2Cl_5 crystal, which belongs to the same space group [10]. However to the best of our knowledge numerical data of polarization properties of RPC refractive index is unknown, refractive index for unpolarized light n_0 and an arbitrary oriented crystal is as high as 2.12 [7].

Single crystal doped with Dy^{3+} ions was grown by the vertical Bridgman method in the two-zone furnace in a silica tube crucible. Crystal growth was started in random crystallization direction, so crystallographic orientation of the sample was arbitrary. Concentration of Dy^{3+} ions in the crystal investigated was determined ICP-MS method and was found to be $1.3 * 10^{-19}$ cm^{-3}.

3. Laser setup

In all experiments we used a Ti:sapphire laser system with a regenerative amplifier operating at wavelength of 0.8 μm. Repetition rate was 1 kHz, and pulse duration τ_{FWHM} at FWHM was

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110 fs. M^2 parameter of laser beam did not exceed 1.05. Motorized polarization attenuator controlled energy of the pulse entering the sample.

4. Non-linear refractive index

Z-scan technique is widely acceptable method for non-linear refractive index measurement [11–14]. The standard scheme of the Z-scan was exploited in our study [11]. We measured transmittance of a plane-parallel plate of the RPC:Dy crystal as a ratio of the input pulse energy E_{in} to the output pulse energy E_{out} in dependency of position of the sample relative the focusing lens with focal distance of 200 mm. The beam waist radius ω_{01} after focusing lens was as small as 45 µm, and the diffraction length $\pi n_0 \omega_{01}^2 / \lambda = 17$ mm. The plate of the RPC:Dy crystal with thickness of 3.8 mm was mounted on a high precision translation stage that translates the plate along the laser beam through the region of beam waist with constant speed of 1 mm/s. Two types of measurement scans were produced, that are with and without an aperture in front of the energy meter head. Transmittance of the aperture itself was as low as 20%. The transmittance of the sample with aperture was normalized on the transmittance without aperture in order to exclude the effect of multiphoton absorption on final results. Typical normalized transmittances at selected input energies (Z-scans) as well as measurements without aperture are presented in Fig. 1. Transmittance change from valley to peak $\Delta T_{p\text{-}v}$ obtained with the aperture is easy measurable value that characterizes Kerr non-linearity.

Because of fast response of Kerr non-linearity in comparison with pulse duration, the non-linear refractive index change $\Delta n(t)$ adiabatically follows the pulse intensity $I(t)$, and the averaged over pulse duration non-linear phase shift $\langle|\Delta\Phi(t)|\rangle$ on the optical axis can be defined as:

$$\langle|\Delta\Phi(t)|\rangle = k_0 d \langle|\Delta n_0(t)|\rangle = \frac{\int_{-\infty}^{\infty} \Delta n_0(t) I_0(t) dt}{\int_{-\infty}^{\infty} I_0(t) dt}, \tag{1}$$

where k_0 is wavenumber in free space, d is the plate thickness. According to numerical approximations made in [11] the averaged phase shift $\langle|\Delta\Phi(t)|\rangle$ is linearly related with transmittance change ΔT_{p-v} and for $\langle|\Delta\Phi(t)|\rangle < \pi$ is calculated within a ±2% accuracy according to formula:

$$\langle|\Delta\Phi(t)|\rangle = \frac{\Delta T_{p-v}}{0.406(1-S)^{0.25}}, \tag{2}$$

where S is the aperture transmittance. This formula and experimental data (such as shown in Fig. 1) allowed obtaining the dependence presented in Fig. 2.

In consideration that laser pulses have Gaussian time profile the averaged refractive index changes $\langle|\Delta n(t)|\rangle$ relates with peak refractive index change Δn_0 according to formula:

$$\langle|\Delta n(t)|\rangle = \frac{\Delta n_0}{\sqrt{2}}, \tag{3}$$

Then Kerr non-linear coefficient γ is retrieved according to its definition:

$$\Delta n_0 = \gamma I_0, \tag{4}$$

where I_0 is peak pulse intensity at the optical axis. In the case of Gaussian pulse in space and time it is connected with pulse energy E_{in} through relation:

$$I_0 = 2\sqrt{\frac{\ln 2}{\pi}} \frac{E_{in}}{\pi \omega_{01}^2 \tau_{WFHM}}. \tag{5}$$

Non-linear refractive index n_2 is related with non-linear coefficient γ by formula:

$$n_2[\text{esu}] = (cn_0/40\pi)\gamma[\text{m}^2/\text{W}], \tag{6}$$

where c[m/s] is speed of light in vacuum.

Formulas (1)–(5) linearly connect phase shift $\langle|\Delta\Phi(t)|\rangle$ with the input pulse energy E_{in}. The dependence obtained from experimental data (Fig. 2) satisfies this rule, so as the restriction $\langle|\Delta\Phi(t)|\rangle < \pi$, up to as high pulse energy as 50 nJ. There is pronounced deviation from linear dependence at higher input energies, and correspondent distortions of Z-scan curves are noticed (Fig. 1). It is obviously due fall out of Gaussian beam approximation due to huge no-linear phase shifts.

Data presented in Fig. 1 and formulas (1)–(5) allow to calculate $\gamma = 4.0 * 10^{-6}$ cm^2/GW. Then according to (6) $n_2 = 2.0 * 10^{-12}$ [esu]. In order to verify numerical accuracy of our experimental procedure we have performed measurements under the same conditions for a plate of fused silica with thickness of 1.1 mm. We have found that for fused silica $\gamma = 1.9 * 10^{-7}$ cm^2/GW, and $n_2 = 6.7 * 10^{-14}$ [esu]. This value is within 20% accuracy coincides with the result obtained by three wave mixing technique [15]. Thus we have found that Kerr-non-linearity of RPC crystal is of factor 21 higher than that of fused silica. Although the defined non-linear coefficient is lower than the typical parameters of other promising

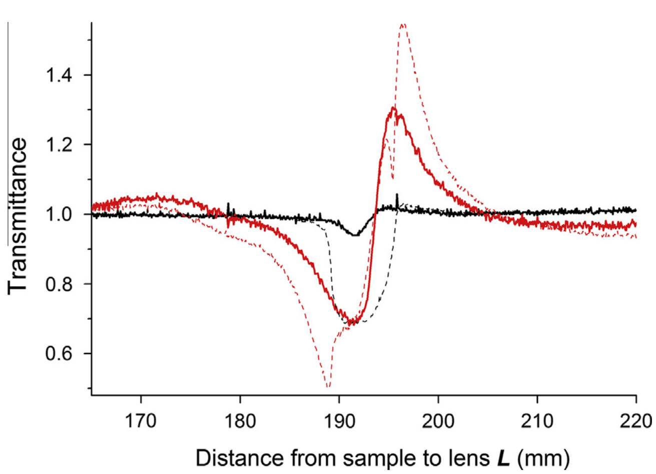

Fig. 1. Transmittance of the sample in dependency on its position along the optical axis with aperture (red lines) and without aperture (black lines). Solid lines: E_{in} = 28 nJ, dashed lines: E_{in} = 70 nJ. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

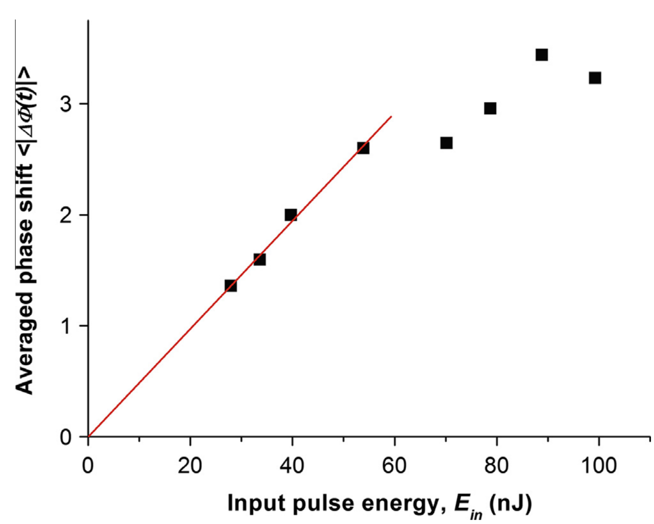

Fig. 2. The averaged phase shift on the optical axis in dependency on the pulse energy entered the crystal (Fresnel reflection is taken into account).

mid-IR materials, such as chalcogenide glasses (for example, it is $3*10^{-4}$ cm^2/GW for As_2Se_3 [16]) and ZnSe crystal ($3*10^{-5}$ cm^2/GW [14]), the advantage of RPC crystal is its large band gap that permits to use it under higher intensities without restrictions coursed by multiphoton absorption. Even diamond, which is an important wide band gap mid-IR material, has lower non-linear coefficient γ equaled to $1.3*10^{-6}$ cm^2/GW [17].

5. Multiphoton absorption

Measurement technique for multiphoton absorption (MPA) and further math treatment of experimental data were identical to those used in our previous paper [18]. The measurement was done under focusing the laser beam by Mitutoyo 100× micro-objective with numerical aperture NA = 0.55 and focal distance of 2 mm in the volume of crystal. In first step the laser beam was focused on the front crystal surface that was controlled by a reflected image of the beam spot, and then the crystal plate was shifted towards laser by distance of 100 μm. Thus the beam was focused in the crystal at depth of about 100 μm × n_0 = 210 μm. Calculated beam waist radius ω_{02} in Gaussian approximation was as low as 0.6 μm. Experimental dependence of transmittance of femtosecond pulses upon input pulse energy is presented in Fig. 3. No visible material modifications was observed for the pulse energies range shown in Fig. 3, The dependence have not any hysteresis and is completely reproducible when pulse energy goes up and down. Spreading of the measured transmittance is caused exclusively by electronic noise.

Note that Kerr non-linearity can be neglected under these experimental conditions, as pulse pick power does not exceed 50 kW, which is lower than critical power for self-focusing of Gaussian beam $P_{cr\_G} = \lambda^2/(2\pi n_0\gamma)$ = 119 kW [19]. Thus we can consider that the beam shape is only controlled by diffraction, and it keeps Gaussian form during focusing. Under these conditions an analytical formula for MPA can be implemented [18]:

$$
\begin{aligned}
&T(E_{in}) = T_0(1 + (K-1)a(K)E^{K-1})^{-\frac{1}{K-1}} \\
&a(K) = \beta_K \cdot \left(\tfrac{2}{\pi}\right)^{3/2\cdot(K-1)} \cdot \frac{\pi\cdot\mu(K)\cdot n}{K^{3/2}\cdot\lambda\cdot\tau_p^{K-1}} \cdot \frac{1}{\omega_{02}^{2\cdot(K-2)}} \\
&K = \{3,4,5\} \\
&\mu(K) = \{\tfrac{\pi}{2}, \tfrac{3}{8}\pi, \tfrac{5}{16}\pi\}
\end{aligned} \quad (7)
$$

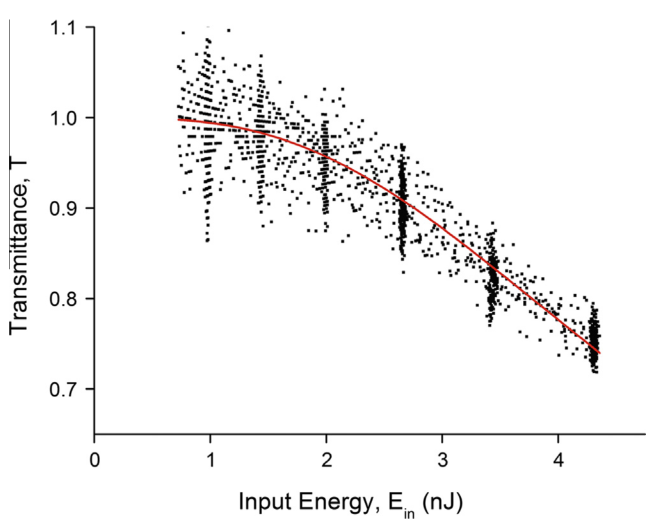

Fig. 3. Measured non-linear transmittance of RPC:Dy crystal (points), and theoretical fitting by formulas (7) (solid line) in dependency upon the pulse energy entered the crystal.

where K is MPA order, β_K is MPA absorption coefficient of the K-th order, $2\tau_p$ is laser pulse width at $1/e^2$ intensity level. Series of numerical fittings to experimental data were done by formula (7) separately for K = 3, 4, 5, while parameters $a(K)$ was varied. The best fit was obtained for K = 4. After fitting of the parameter $a(K)$ we found that $\beta_4 = 2.3*10^{-34}$ cm^5/W^3.

Energy gap for RPC crystal was estimated to be as high as 4.83 eV [20]. Our result K = 4 well corresponds to this value, as four photon excitation (with energy of $4hc/\lambda$ = 6.2 eV) throws over an electron from valence to conduction band, while energy of three photons ($3hc/\lambda$ = 4.65 eV) is insufficient to excite an electron to the conduction band.

6. Permanent refractive index change

Experiments on femtosecond modification were done under conditions close to MPA measurements. Astigmatic focusing was used in order to diminish destructive influence of self-focusing [12]. In order to provide the astigmatic focusing a cylindrical lens with focus distance of −34 cm was placed in front of Mitutoyo lens. This way we produced inside the crystal two elliptical beam waists instead of one circular waist. Large and small diameters of the ellipse nearest to Mitutoyo lens were calculated to be equal to 1.1 μm and 14 μm correspondingly (at $1/e^2$ level of intensity). Focusing depth in the crystal was controlled by the same manner and was close to those used in MPA measurements. Unlike MPA measurements permanent modification of the crystal was accompanied by translation of crystal with constant velocity V = 0.5 mm/s in direction perpendicular to laser beam and along the big axis of elliptical beam waist nearest to Mitutoyo (there are two beam waists due to astigmatic focusing). Inscribed tracks were investigated on Axioscope Zeiss microscope. End view of typical tracks is shown in Fig. 4. 2-D distribution of phase delay for light passing the modified region of the crystal along the same direction as the laser beam went was measured by QPm method [21]. Being normalized on track height (the size in direction of the inscribing laser beam) it becomes a patterning of refractive index change. Typical tracks of modified refractive index are presented in Fig. 5. Refractive index change is negative in RPC crystal, which is typical for femtosecond modification in crystals.

Dependence of maximal refractive index change in a track together with the track height upon input pulse energy is presented in Fig. 6. Inscription threshold was found to be as low as 0.2 μJ. There is rather sharp decrease in refractive index above the thresh-

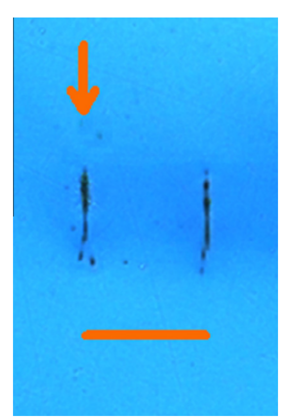

Fig. 4. Microscopic bright field image of ends of pair tracks inscribed when a sample was translated in mutually opposite directions. The arrow shows direction of the inscribing beam. Pulse energy entering the crystal E_{in} = 0.38 μJ. Size of scale bar is equaled to 50 μm.

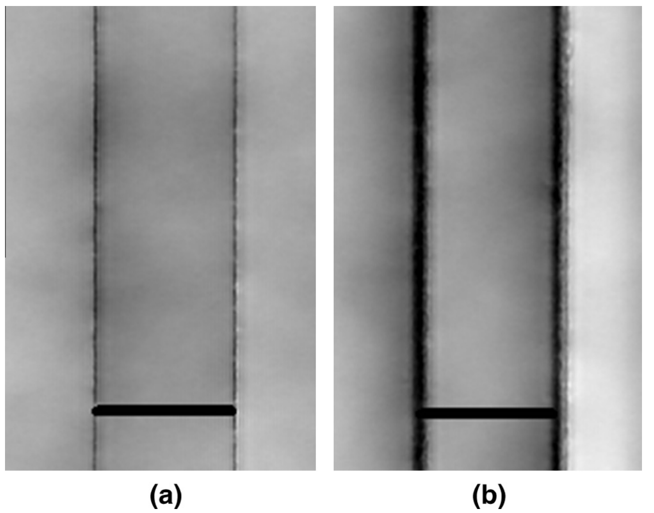

Fig. 5. 2-D phase distribution after inscribing of pair tracks in mutually opposite directions. $V = 0.5$ mm/s. (a) $E_{in} = 0.38$ μJ and (b) $E_{in} = 2.1$ μJ. Size of scale bar is equaled to 50 μm.

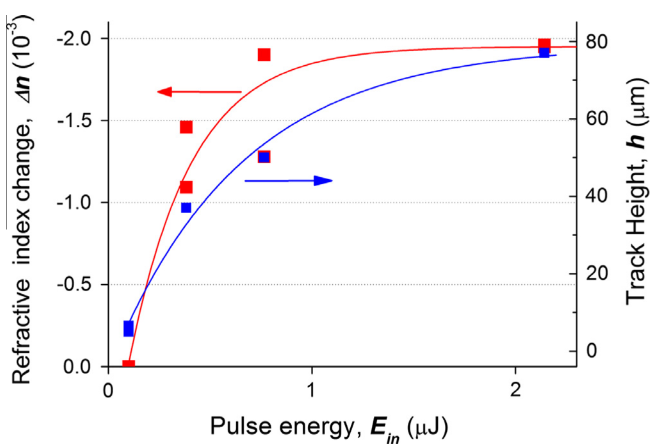

Fig. 6. Dependences of permanent refractive index change Δn (red points) and track height h (blue points) upon the pulse energy entered the crystal (Fresnel reflection is not taken into account). Solid lines serve for eye guide only. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

old, and then the index change saturates near $-2 * 10^{-3}$ at input energy level about of 1 μJ.

It is interesting to estimate role of self-focusing in the inscription process. Convenient criteria in this concern is the critical area of a circular beam waist below which self-focusing is unavoidable [19]:

$$S_{cr} = \frac{P_{cr\_G}}{I_{insc}}, \tag{8}$$

where I_{insc} is intensity at the threshold of inscription. The measured energy threshold and area of astigmatic beam waist calculated in diffraction approximation allow to define that $I_{insc} = 1.4 * 10^{13}$ W/cm^2. Then we obtain that $S_{cr} = 0.9$ μm^2. Comparing with calculated Gaussian beam waist area of 1.1 μm^2 produced by Mitutoyo lens, we come to conclusion that self focusing plays significant role in inscription process in RPC crystal by pulses of 100 fs duration. Astigmatic focusing increases the critical power [22,23], and consequently diminishes instabilities associated with self-focusing. Thus we consider that the astigmatic focusing producing an elliptical beam waist is a key element for inscription of smooth tracks in RPC crystal.

7. Conclusion

We have demonstrated laser inscription of tracks in RPC:Dy single crystal with permanent negative refractive index change under exposer of 110-fs pulses at wavelength of 800 nm and repetition rate of 1 kHz. Maximal module of refractive index change was found to be as high as $2 * 10^{-3}$. Fourth order multiphoton absorption process was found to be responsible for non-linear absorption of the femtosecond pulses and initiating the inscription process. Kerr non-linear coefficient was measured, and found to be factor of 21 higher than that in fused silica. We found that the self-focusing plays an important role during the inscription in RPC crystal, and special care should be taken in order to diminish its contribution, when waveguides will be written in this crystal. RPC crystal has both high non-linear refractive index and wide band gap, and such combination of the parameters makes it attractive for mid-IR non-linear photonics.

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