Increasing the laser damage threshold of the Nd:YAG crystal by the color center annihilation

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Abstract. This paper presents increase in laser damage threshold of the Nd:YAG crystal subsequent to annihilation of oxygen vacancies in the crystal structure at low dose of XeCl laser irradiation. A Nd:YAG crystal was irradiated with 500 pulses of XeCl laser (λ=308nm, τ=20 ns) at the fluence of ~100 mJ/cm² and 25 Hz repetition rate. The optical absorptions of the Nd:YAG crystal reduced in ultraviolet and visible regions due to elimination of some color centres indicated by UV-Vis-NIR spectra. We measured the laser damage threshold of the irradiated and un-irradiated crystals using 30 ns, 1064 nm single longitudinal mode, TEM₀₀ pulses of a passively Q-switched Nd:YAG laser. The laser damage threshold of the irradiated crystal (after dividing by √3 to scale for pulse duration of 10 ns) was obtained to be 501±50 mJ/cm². It is nearly 5 times as high as that of un-irradiated Nd:YAG crystal, which was found to be 102±15 J/cm². The present results are very important for using Nd:YAG crystals as the laser amplifier media.

1. Introduction
Damage is a problem that optical materials are encountered when exposed to laser irradiation. As a result, solid state laser materials and optical components of laser systems are damaged due to the laser irradiation effects. By increasing the application of high peak power lasers, it is necessary to high quality laser components and active media be used in the laser systems.

Experimentally measured laser induced damage threshold (LIDT) of the most of the optical and laser active materials is much less than the intrinsic LIDT of them [1]. The parameters involved in damage phenomena have been studied extensively and some responsible factors have been mentioned. They include inclusions [2], impurities [3] and intrinsic point defects [1].

For high purity good polished laser crystals, point defect factors can be important due to the uncontrolled and unintentional incorporation of some definite point defects during the growth process. The most important point defects of the Nd:YAG crystal structure are oxygen vacancy and its related defects. With growing Nd:YAG crystal in vacuum or argon and nitrogen gas atmosphere, many oxygen vacancy centers are formed in the ordered crystal structure due to the absence of sufficient oxygen ions. Each oxygen vacancy by trapping an electron can be changed to F⁺ center. Similarly, each F⁻ center defect can capture another electron to form a neutral center named as F center. These defects have several absorption bands in the UV-Vis-NIR spectral region. In general, these defects are
named as colour centers due to absorption of light in the visible spectrum such that a material that is usually transparent becomes coloured. With having energy states in the band gap, they couple to the laser irradiation, strongly absorb laser energy, enhance laser materials interaction and finally lead to damage of the materials.

In this paper, a Nd:YAG crystal sample was irradiated by low dose XeCl laser irradiation in the ambient air for removing some oxygen vacancies and related defects of the crystal structure. Modification of the defect structure is studied by additional absorption spectrum of the irradiated sample. Then, LIDT of un-irradiated and the irradiated samples are measured by a 1064 nm polarized Gaussian single longitudinal mode of a passively Q-switched Nd:YAG laser system and compared with each other. Nearly 5 times higher LIDT of low dose XeCl laser pre-irradiated sample was obtained in the present work that is an important result for using Nd:YAG crystals as an amplifier media.

2. Experiments
A Nd:YAG single crystal (1 at.% Nd\(^{3+}\)) was grown in an iridium crucible along the [111] crystallographic direction by the Czochralski method under Ar atmosphere. The crystal was cut into thin discs of 12.5 mm in diameter and 2.4 mm in thickness. The disc samples were polished on both sides (≤ λ/4@632.8 nm flatness) and cleaned by sulfochromic acid and deionized water at ultrasonic chamber.

A Nd:YAG crystal sample was irradiated by 500 pulses of XeCl excimer laser system (Lambda Physik X200, \(\lambda=308\) nm, \(\tau=20\) ns) at the fluence of ~100 mJ/cm\(^2\) and 25 Hz repetition rate. Irradiations were performed perpendicular to the crystal surface in the environmental condition with the 300 mJ laser output energy and 30×10 mm\(^2\) spot size.

The optical absorption spectra of the samples were recorded by a (Cary 500) UV-VIS-NIR Spectrophotometer (200-900 nm) before and after the irradiation. Defects in oxide crystals can be studied by optical absorption spectrum. Change of the defect energy state leads to new optical absorption\(^[4]\).

To determine the type and amount of changes in defect structure, the value of laser induced additional absorption (AA) is calculated by \(^[5]\):

\[
\Delta k = \frac{\ln(T_1 / T_2)}{d}
\]

Where \(k\) is the absorption coefficient, \(d\) is the sample thickness; \(T_1\) and \(T_2\) are the crystal transmission before and after the laser irradiation, respectively.

After XeCl laser irradiation, effect of the irradiation on the LIDT of the Nd:YAG crystal sample was examined experimentally. The laser induced damage threshold experimental setup is illustrated schematically in Figure 1. Laser system delivered a passively Q-switched single longitudinal mode, TEM\(_{00}\) Gaussian-shaped laser beam at a wavelength of 1064 nm with a pulse width of 30 ns FWHM. The beam profile was nearly perfect TEM\(_{00}\), and the polarization was linear. The experiments were performed according to the “1-on-1” standard testing method for single shot damage measurement in laboratory environmental conditions. Then, each site received only one pulse, for each of which the pulse width and pulse energy were monitored.
Figure 1. The experimental setup of 1064 nm Nd:YAG laser induced damage threshold measurement, where M, are mirrors, ET, are etalons, PD is a photodiode, QWP is a quarter wave plate, HWP is a half wave plate, BS is a beam splitter, DP is a Dove prism, BM is a back mirror, AM is the active medium and AMP is the amplifier.

Damage was identified by visually observing a laser spark and scattering of a coaxial He–Ne laser probe beam focused on the irradiated site that is collinear with the path of the 1064 nm beam. Onset of the damage was clearly visible due to the scattering of the probe beam. Occurrence of damage was confirmed afterward by observing the irradiated sites under an optical microscope. Increasing the lens focal length reduces statistical variability and allows more accurate determination of the LIDT of materials. Thus, we used a 400 mm focal length lens with antireflection coatings on the both surfaces. The spot size of the beam incident on the sample was 90±10 μm diameters at 1/e^2 of the maximum intensity. The sample front face was placed on 12 mm behind the focal point of the lens. Damage locations were laterally separated by about 1 mm.

3. Results and discussion
Figure 2 shows the UV-Vis optical transmission spectra of the Nd:YAG sample before and after the irradiation. As seen, the optical transmission has increased after XeCl laser irradiation. It has been shown that increase and decrease of optical absorption in the entire spectral range are the characteristic features of generation and annihilation of point defects in the materials, respectively [6]. Thus, it seems some point defects can be annihilated during the laser irradiation.

To determine the type and value of XeCl laser induced annihilated defects, additional absorption (AA) spectrum of the Nd:YAG sample was obtained. Figure 3 shows the AA spectrum in which a broad negative AA band at 236 nm is observed. There are also some tiny negative bands that are corresponded to Nd^{3+} absorption bands. It is known that oxygen vacancy is the main defect of the Nd:YAG crystal structure[7], so it is proposed that the 236 nm big negative band can be related to the annihilation of many oxygen vacancy centers.

On the other hand, it is known that annealing at high temperatures improves optical features of oxide crystals by removing some oxygen vacancy centers[8]. Thus, in order to find the oxygen vacancy related absorption band we annealed another Nd:YAG sample in the air for 3 hours at 400°C for thermal relaxation and then 3 hours at 1100°C for changing the defect structure. The optical spectrum was recorded before and after annealing and then the AA spectrum of the annealed sample was obtained.
Figure 2. Transmission spectra of the irradiated (100 mJ/cm$^2$, 500 pulses, 25 Hz) and un-irradiated Nd:YAG crystal sample.

Figure 3. Additional absorption spectrum of the XeCl laser irradiated Nd:YAG sample (100 mJ/cm$^2$, 500 pulses, 25 Hz).

Figure 4 shows the AA absorption spectrum of the annealed Nd:YAG crystal with the broad absorption band centred at 256 nm, which has been observed in air annealed Nd:YAG and YAG crystals[4]. It has been attributed to charge transfer from oxygen ion to Fe$^{3+}$ ion. Generally, some uncontrolled Fe$^{3+}$ and Fe$^{2+}$ ions often exist as impurities in Nd:YAG crystals. XRF analysis also detects about 400 ppm of iron ions in the Nd:YAG crystal samples which were used in the
experiments. Some oxygen vacancies can be filled by oxidizing Fe$^{2+}$ impurity during annealing in the air and then the number of Fe$^{3+}$ ions localized near the oxygen ion will increase.

![Graph](http://example.com/graph.png)

**Figure 4.** Additional absorption spectrum of the annealed sample (for 3 hours at 400°C and then 3 hours at 1100°C).

In addition, Figure 4 shows a sharp negative absorption band at 236 nm that has not been reported earlier to the best of our knowledge. As mentioned above, annealing removes some oxygen vacancies in the Nd:YAG crystals and annihilation of the point defects creates negative bands in additional absorption spectrum. Then, there should be a negative band related to the annihilation of the oxygen vacancies in the additional absorption spectrum of the annealed sample, but it is observed no negative band in the additional absorption spectrum except the 236 nm negative absorption band. Thus, we can conclude that the 236 nm negative band is just related to the annihilation of the oxygen vacancy center.

Therefore, the 236 nm absorption band in additional absorption spectrum of the XeCl laser irradiated Nd:YAG sample is also related to the annihilation of the oxygen vacancy centers in Nd:YAG crystals.

To study the effect of the oxygen vacancy annihilation in LIDT of the Nd:YAG crystal, we measured the LIDT of the XeCl laser irradiated and un-irradiated Nd:YAG crystals at different lateral positions by gradually increasing the pulse energy at each location until optical breakdown occurred. Experiments were repeated several times and the results were averaged. The threshold fluence for un-irradiated crystal after dividing by $\sqrt{3}$ to scale for pulse duration of 10 ns was found to be $102\pm15$ J/cm$^2$.

The LIDT of XeCl laser irradiated Nd:YAG crystal scaled for pulse duration was obtained to be $501\pm50$ mJ/cm$^2$ that is nearly 5 times as high as that of un-irradiated Nd:YAG crystal.

According to the present results, we can conclude that the oxygen vacancy annihilation increases the LIDT of the Nd:YAG crystal. Therefore, the oxygen vacancy is an important defect responsible for LIDT phenomenon in the Nd:YAG crystal. Indeed, oxygen vacancies can act as electron traps. When an oxygen vacancy captures one electron, it forms F$^-$ center. Also, F$^-$ center can capture another electron and change to natural vacancy named F center. These defects, which are generally called color centers, have several absorption bands in the spectral range of UV-Vis-NIR spectral range.
In high power laser interaction with Nd:YAG crystal, multi-photon absorption can ionize or excite electron to the conduction band, then many O hole centers produce and any trapping centers such as oxygen vacancy capture free electrons. Consequently, the defect structure in the crystal gradually changes and new defects appear with the new optical absorption bands. In this condition, the effective energy absorption of the crystal and also the coupling between the laser irradiation and the crystal increase till the breakdown happens in the crystal. If no trapping center such as oxygen vacancy exists in the crystal structure, the generated electrons and hole centers can recombine together and no new defects that can lead to damage would be generated in the crystal structure. Therefore, oxygen vacancies of Nd:YAG crystal structure help to onset of laser damage in the Nd:YAG crystal, so annihilation of the oxygen vacancies by low intensity XeCl laser pre-irradiation can increase the LIDT of the Nd:YAG crystal.

4. Conclusions
In conclusion, we presented five times higher laser induced damage threshold following pre-exposure to 100 mJ/cm² sub-threshold XeCl laser irradiation due to annihilation of the oxygen vacancy centers. The threshold fluences for un-irradiated and XeCl laser irradiated crystal after dividing by √3 to scale for pulse duration of 10 ns were obtained 102±15 and 501±50 J/cm², respectively.

We demonstrated the important role of oxygen vacancy centers, the most important Nd:YAG crystal defect, on laser induced damage of the Nd:YAG crystal for the first time to the best of our knowledge.

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