

## Formation of Permanent Brown-colored Patterns in Transparent BK7 Glass upon Irradiation with a Tightly Focused Femtosecond Laser

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### Research Article

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#### ABSTRACT

Transparent borosilicate glass (BK7) is extensively used in optics applications. Herein, we demonstrate that a brown-colored pattern is generated inside BK7 glass upon irradiation with a near-infrared Ti:sapphire femtosecond laser and reveal the importance of maintaining the laser power at values well below the BK7 damage threshold for color center formation. The use of low laser power prevents the occurrence of mechanical damage (e.g., micro-crack or thread formation) in the generated colored area, and Gaussian fitting of the absorbance spectrum of BK7 shows that this material exhibits a band gap of 4.21 eV with three absorption edges. Thus, the developed patterning method is expected to find numerous applications in the future color processing of lines and points in glass.

#### INTRODUCTION

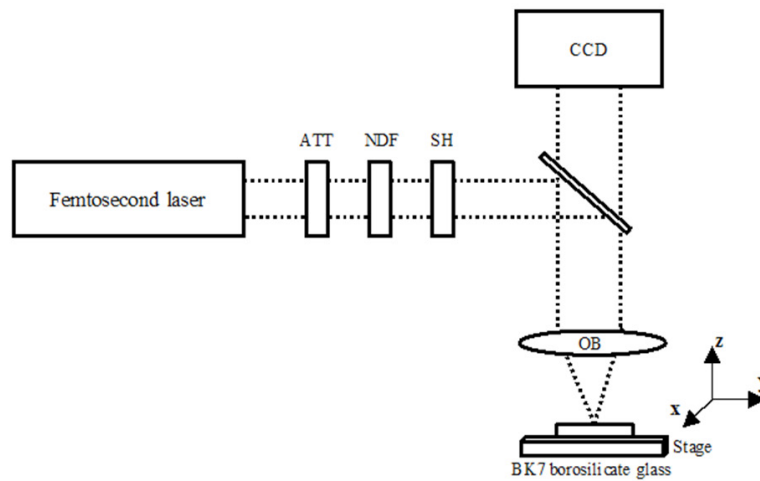
BK7 glass (aka Pyrex) is a borosilicate glass featuring an amorphous network of interconnected triangular  $\text{BO}_3$  and tetrahedral  $\text{SiO}_4$  units. The high visible-light transparency, minimal thermal expansion, chemical stability, and low foam content of BK7 glass make it a popular material for the fabrication of optics such as prisms and lenses and account for its frequent use as optical fiber cladding because of its lower refractive index compared to those of other types of glass <sup>[1]</sup>.

Although BK7 glass appears colorless and transparent when exposed to visible or lower-energy light, color centers can be formed upon its exposure to high-energy (several  $\text{GW}/\text{cm}^2$ ) electromagnetic radiation such as gamma rays, X-rays, and UV laser beams. The formation and disappearance of color centers under these conditions have been studied for several decades, and the development of femtosecond lasers in the 1990s has made the contactless injection of colors into clear glass much easier <sup>[2]</sup>. However, color modification based on ultrafast laser irradiation has not been extensively explored up to now <sup>[3]</sup>, and hardly any research has been conducted on the mechanism of color modification resulting from the interaction of femtosecond photons and transparent materials.

Herein, we show that irradiation with a near-infrared Ti:sapphire femtosecond laser resulted in the formation of a brownish pattern inside high-purity transparent BK7 glass. The above pattern was characterized by linear absorption spectroscopy, and Gaussian fitting was performed to demonstrate the stability of this pattern at room temperature for an extended period of time as well as to reveal the formation of impurity-free color centers.

## EXPERIMENTAL SETUP

A femtosecond laser beam was focused into BK7 glass to generate a brown-colored pattern inside the same, with the experimental setup schematically shown in **Figure 1**.



**Figure 1.** Schematic representation of the machining system used for irradiating BK7 glass with a femtosecond laser (ATT: Attenuator, NDF: Neutral Density Filter, SH: Shutter, OB: Objective Lens, CCD: Charge coupled device)

A diode-pumped Nd:YVO<sub>4</sub> laser was used as the seed, and laser pulses were stretched and amplified using a Ti:sapphire regenerative multipass amplifier (Quantronix, Titan amplifier). A mode-locked Ti:sapphire laser (Quantronix, Integra system) with a wavelength of 800 nm, a pulse duration of 130 fs, and a repetition rate of 1 kHz was utilized for color formation. The laser beam was set up to focus inside the transparent BK7 glass by passing through a 0.15 numerical aperture (NA) objective lens. A stage was constructed to operate within a 50 nm error range in the x-, y-, and z-axis directions to ensure machining accuracy.

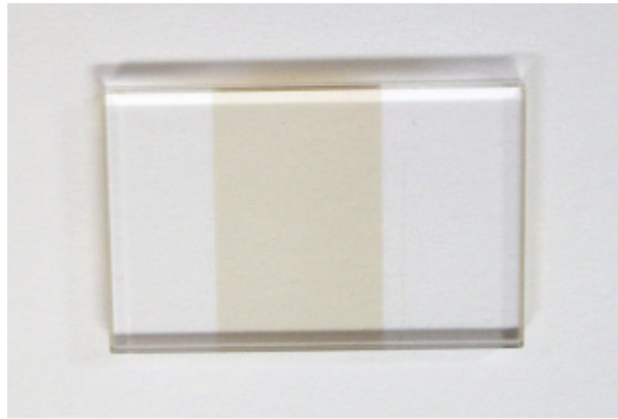
The femtosecond laser beam was focused at a depth of 200 μm from the glass surface at a laser power of 17 mW using a 0.15 NA objective lens, and the (rather wide) brown-colored pattern was produced at a scan speed of 0.5 mm/s (**Figure 2**).

Although Efimov et al.<sup>[3]</sup> succeeded in line-patterning the surface of borosilicate glass utilizing a femtosecond laser at a power below the glass damage threshold, they found that this approach was poorly suited for the formation of free patterns. However, the intensity of the laser beam used herein ( $0.8 \times 10^{12}$  W/cm<sup>2</sup>) was reduced by a neutral density filter so that internal permanent coloring could be performed even if the laser beam focus reached inside the borosilicate glass, the internal damage threshold of which was confirmed to equal  $10^{12}$  W/cm<sup>2</sup>.

Patterned BK7 was characterized by optical microscopy, which allowed the spacing between the filled lines of the colored area to be determined as 15 μm and showed that no cracks or threads were formed in the patterned area. In addition, room-temperature absorption spectra of the generated color pattern were acquired using a UV-VIS spectrometer (Shimadzu, UV-2450), and the color of this pattern was confirmed by visual observation under fluorescent and halogen lamps.

## RESULTS AND DISCUSSION

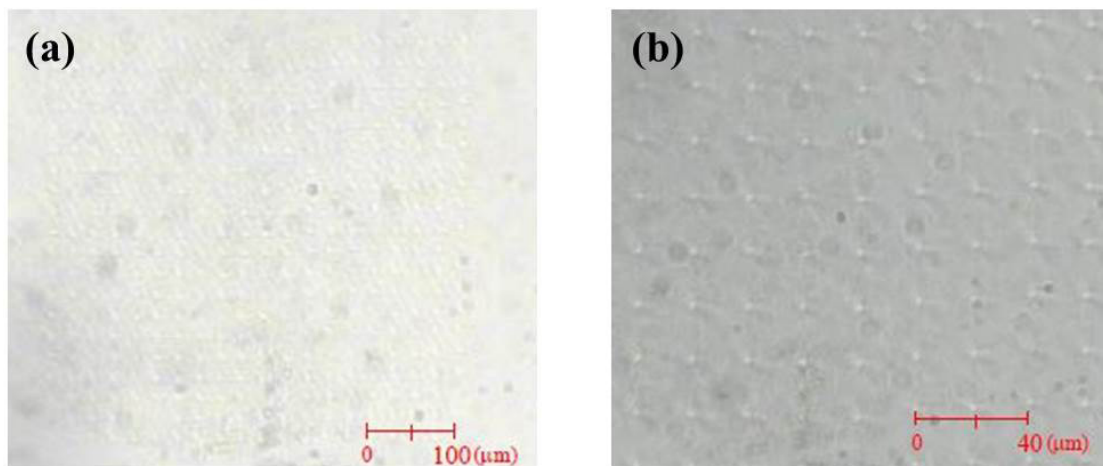
Optical microscopy imaging revealed that laser irradiation did not result in the formation of any cracks or threads in the patterned area (**Figure 2**).



**Figure 2.** Image showing a brown-colored pattern in bulk BK7 obtained by femtosecond laser machining.

Periodically arrayed structures of modified bulk were fabricated by scanning a planar BK7 plate using variable-intensity irradiation and optical X–Y–Z stages (**Figure 2**). The depth of such periodically arrayed structures equaled 1.0 mm from the irradiated surface of the plate.

The generation of modified-refraction-index periodic structures (diameter  $\approx 2 \mu\text{m}$ , pitch =  $20 \mu\text{m}$ ) was ascribed to low-density plasma formation ( $n_e < 1.79 \times 10^{27} \text{ m}^{-3}$ ) upon single-shot irradiation at  $5 \times 10^{13} \text{ W/cm}^2$  (**Figure 3a**). Additionally, periodic structures with optical cracks (diameter  $\approx 8\text{--}13 \mu\text{m}$ , pitch =  $20 \mu\text{m}$ ) were also produced, which was ascribed to the formation of solid-density plasma ( $n_e > 1.79 \times 10^{27} \text{ m}^{-3}$ ) upon single-shot irradiation at  $4 \times 10^{14} \text{ W/cm}^2$  (**Figure 3b**). Notably, no optical damage or laser ablation on the surface of the BK7 substrate were observed after laser irradiation in both cases, which implied that low-density plasma formation upon irradiation by tightly focused femtosecond beams would be useful for fabricating modified-refractive-index internal gratings in BK7 plates.



**Figure 3.** Two types of modified-refractive-index internal gratings fabricated by scanning planar BK7 plate using an optical stage: (a) dot structure; (b) linear structure.

The linear absorption characteristics of pristine and laser-irradiated BK7 glass were evaluated and compared in the range of 1.5–4.0 eV. The 4 eV range was avoided, since it approached the band gap energy of  $\text{B}_2\text{O}_3\text{-SiO}_2$  glass. The absorption spectra of the brown-colored pattern and unpatterned BK7 glass were compared to observe the light absorption characteristics specific to the area of color center formation. The former spectrum was fitted with three Gaussian curves (with maxima at 1.93, 2.24, and 2.81 eV) and an absorption edge corresponding to the band gap, which allowed the band gap energy of BK7 glass used in this experiment, obtained by Gaussian fitting, was 4.21 eV, and the color centers formed from exposure to the femtosecond laser were estimated to be near 1.93 eV, 2.24 eV, and 2.81 eV, respectively [4].

The pattern formed was confirmed to be brown in color when observed under both fluorescent and halogen lamps.

Although the modification/microfabrication of transparent materials by ultrafast photons has been extensively investigated [5-10], the color change of transparent materials due to their interactions with such photons has been underexplored, since the

use of conventional nanosecond pulse lasers results in the generation of cracks in the irradiated area without any color change. As a result, any research into applications based on color changes was impossible. Therefore, this work is particularly important, as it demonstrates the potential of utilizing laser powers below the material damage threshold for selective color modification in transparent glass (BK7).

### CONCLUSIONS

Herein, a Ti:sapphire femtosecond laser with a wavelength of 800 nm was used to produce brown-colored areas inside transparent BK7 glass. Notably, according to the results of optical microscopy imaging, this irradiation did not result in any mechanical glass damage. Gaussian fitting of the measured linear absorption spectrum allowed the band gap energy to be determined as 4.21 eV, and the energies of the three color centers formed by exposure to the femtosecond laser were obtained as 1.93, 2.24, and 2.81 eV, respectively.

During irradiation to form color patterns in BK7 glass, the pulse energy was fine-controlled using a neutral density filter, and a power level below the material damage threshold was used to avoid cracking, which implied that this filtering technique provides a basis for the future color processing of lines and points in glass.

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