Transient absorption in visible region of K9 glass irradiated by nanosecond laser at 355 nm

F. GENG[a,b], J. HUANG[a], Q. Z. LI[a], H. J. LIU[a], F. R. WANG[a,*], X. D. JIANG[a], W. D. WU[a,b]
[a]*Research Center of Laser Fusion, China Academy of Engineering Physics, Mianyang 621900, China*
[b]*Science and Technology on Plasma Physics Laboratory, Research Center of Laser Fusion, Mianyang 621900, China*

Transient optical absorption properties in visible region of K9 glass under nanosecond ultraviolet (UV) laser irradiation (355 nm, 10 Hz) are investigated and discussed. Both the transient absorption spectra and absorption decay properties are presented in this paper. Transient absorption spectrum of K9 glass under UV laser irradiation shows a broad absorption band with maximum at 450 nm and a shoulder at 600 nm. The observed transient absorption bands in K9 glass are suggested to arise from laser induced defects identified as boron oxygen hole centers (BOHC) and non-bridge oxygen hole centers (NBOHC), respectively. Pump-fluence dependency of transient absorption intensity indicates that nonlinear absorption of the pump laser plays an important role in generating such UV-induced hole centers.

(Received June 22, 2016; accepted April 6, 2017)

Keywords: transient absorption, laser irradiation, defect, glass

1. Introduction

K9 glass is an alkali borosilicate with high thermal, chemical and mechanical resistance constituted mainly by SiO_2, B_2O_3 and Na_2O. It is an important and low-cost material that can be used to produce various optical elements such as window, lens, prism and so on. K9 glass is also widely used as coating substrates for reflection, anti-reflection and polarization in laser systems. In high-power laser systems, laser-induced damage problem is a crucial limiting factor that affects the efficiency and operational lifetime of optics [1,2]. Laser-induced damage of K9 glass have been studied by infrared laser at 1.06 μm and far infrared laser at 10.6 μm [3-5]. The damage performance of K9 glass under ultraviolet (UV) laser irradiation has not been explored in-depth. Laser-induced damage in transparent optical materials with wide band-gap is always initiated by precursors like contaminations and structural defects that can response to absorb the incident laser energy [6-10]. Previous studies have shown that point structural defects can be induced in silica during laser induced breakdown and these defects can absorb laser energy to cause damage growth [11,12]. For borosilicate and other glasses, evidences have shown that glass will experience dramatic transparency degradation under irradiations of gamma rays, high-energy electrons and high-intensity UV laser [13-16]. High-energy or high-intensity irradiation will excite electron-hole pairs in glass. The generated carriers have probability to be trapped by glass network to form color centers. The trapped electrons or holes exhibit specific absorption bands which not only decrease the transmission but also can possibly act as damage precursors. Such color centers are meta-stable defects and can be annihilated by recombination processes. In order to study the formation and evolution processes of radiation induced defects, transient optical absorption was adopted to provide both the information of defect type and the decay feature of specific defect. Such investigations have been conducted on glass, fused silica, optical crystals under irradiation of electron pulses or laser pulses [17-21]. However, there is still little report of transient optical absorption study on borosilicate glass under nanosecond UV laser irradiation. In our previous study, we have carried out a single-shot transient absorption measurement of K9 glass, showing broad band absorption under irradiation with sub-damage fluence of about 4 J/cm^2 [22]. In this paper, we will concentrate on the experimental analysis of transient absorption of K9 glass in the visible region excited by relative low fluence nanosecond UV-laser irradiation at 10 Hz. The experiment results indicate that specific hole centers could be produced under nanosecond UV laser irradiation. Decay features at different wavelengths are also investigated to provide information about the temporal evolution of such laser induced defects.

2. Experimental

K9 glass sample in our experiments was cut to a size of 30 mm×30 mm×3 mm and both sides were polished. Before laser irradiation, the sample was washed by ethanol to keep the surfaces clean. The transient optical absorption experiments were performed with a pump-probe configuration as shown in Fig. 1. The pump source is a Q-switched Nd:YAG laser producing 3ω (355 nm) laser pulses with maximum pulse energy about

100 mJ at 10 Hz. The pulse duration of the pump laser is about 7 ns. The energy fluctuation of 3ω pulses is below 3%.

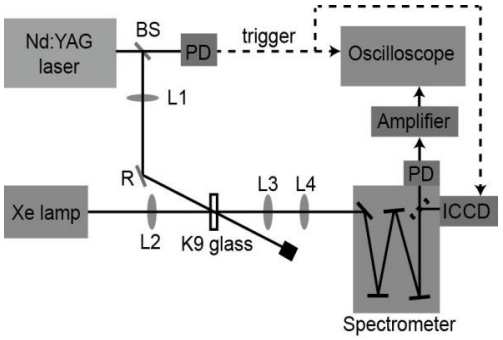

Fig. 1. Schematic of the experimental setup to measure transient optical absorption in K9 glass. BS: beam splitter; PD: photodiode; L: lens; R: reflector

Transient absorption induced by pump laser excitation was probed by a white-continuum beam from a xenon lamp (EQ-1500, Energetiq) with high brightness and stable output (power RMS<0.5%). The probe beam was focused onto the sample with diameter of about 1 mm, while cover the probe spot on the sample. The transmitted probe beam was coupled into a spectrometer (SP500i, Princeton instruments) and then detected by either an intensified CCD (PI-MAX, Princeton instruments) which could provide time-resolved spectra (spectroscopy mode) or a photodiode (S3071, Hamamatsi) with an amplifier circuit that connected to an oscilloscope (HDO4054, Lecroy) to obtain the decay feature of absorption at a specific wavelength (single-wavelength dynamic mode). The detectable wavelength region is 350 nm-900 nm for ICCD and 350 nm~1100 nm for photodiode, respectively. The time resolution of spectroscopy mode and single-wavelength dynamic mode can be down to 5 ns and 50 ns, respectively. Transient optical absorption is expressed as optical density $\Delta OD=log(T_0/T_t)$, where T_0 is the intensity of the transmitted probe light with no pump pulse irradiation, and T_t is the intensity of transmitted probe light at a delayed time t after pump excitation. Both acquired transient absorption spectra and time evolution curve were averaged by repeated measurements in order to improve the signal-noise ratio. In this paper, the average error of absorption change of repeated measurements for transient absorption is about ~5 mOD at spectroscopy mode and ~0.1 mOD at single-wavelength dynamic mode, respectively.

3. Results and discussion

When K9 glass is exposed to UV laser, the glass would experience prominent degeneration after laser irradiation. This phenomenon has been described in previous study, which is believed to be caused by laser-induced structural defects in glasses such as the trapped electron or hole centers [13,14]. In order to investigate the dynamic process under UV laser irradiation, we performed the transient absorption experiments for K9 glass with nanosecond pulsed UV laser irradiation (10 Hz, ~3 J/cm^2). Figure 2 shows time-resolved transient absorption spectra of K9 glass measured by spectroscopy mode. To ensure a sufficient intensity of probe beam detected by ICCD, the gate width of ICCD was set as 1 μs. The spectrum acquired immediately after pump pulse (with 20 ns delay) is shown in Fig. 2(a). The spectrum exhibits an absorption band with a maximum at ~450 nm. A valley with negative ΔOD between 525 nm and 625 nm on the spectrum is also observed. Such valley feature is considered to be the signal of transient fluorescence of defects in K9 glass. Fluorescence signal in this region originates from the superimposed emission bands of oxygen vacancy related defects and non-bridge oxygen hole centers under UV laser irradiation [11,23]. In Fig. 2(d), it is shown that the fluorescence signal decays very fast and is observed to vanish in about several hundreds of nanoseconds, which was measured by single-wavelength dynamic mode. However, the signal of UV laser-induced transient absorption can persist much longer. In Fig. 2(b), the spectrum acquired at a delay time of 100 μs shows a pure absorption feature with a maximum at ~450 nm. Meanwhile, a weak absorption shoulder at ~ 600 nm can be observed. At 1 ms delay, the transient absorption shows a similar spectrum with absorption feature at ~450 nm and ~600 nm but with weaker intensities compared with the transient absorption spectrum shown in Fig. 2(b).

We also measured the decay features of the transient absorption at different wavelengths. Fig. 3(a) shows typical kinetic decay curves of laser-induced transient absorption at selected wavelengths as 450, 500, 550 and 600 nm, respectively. After pump pulse excitation, the induced absorption shows a fast drop in a few milliseconds, followed by a tail extended to tens of milliseconds. In our experiments, the absorption intensity at long wavelength decays faster than short wavelength for the first several milliseconds. But all the curves tend to move together later. In order to further understand the decay feature, the presented decay curves shown in Fig. 3(a) are fitted by a double exponential function: $y=y_0+A_1\exp(-t/t_1)+A_2\exp(-t/t_2)$. The parameters are listed in Table 1. The two fitted time constants are about 1 ms and 20 ms, respectively. But the proportion of the shorter decay component increases with the probe wavelength increasing. It implies that the laser-induced transient absorption at short wavelength can persist longer. Transient optical absorption spectra can also be derived from the decay curves at different probe wavelengths, which are shown in Fig. 3(b). The spectra exhibit very broad band absorption but still with a maximum at ~450

nm and a shoulder at ~600 nm, which is coincided well with the spectroscopy result shown in Fig. 2.

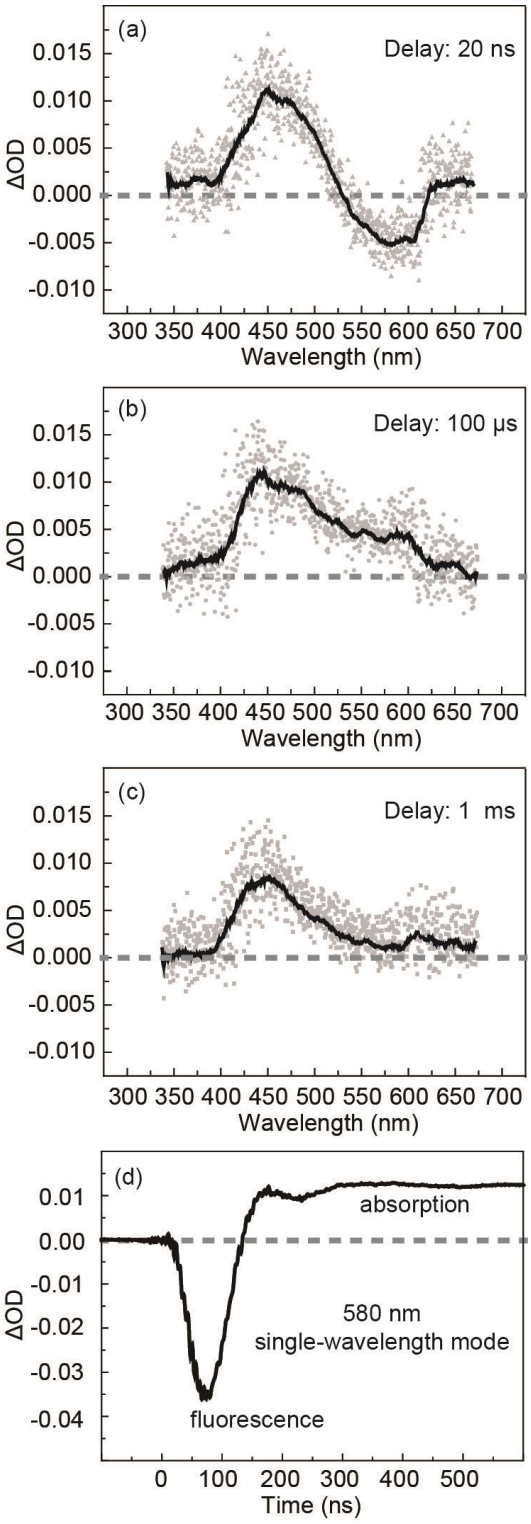

Fig. 2. (a)–(c) Transient optical absorption spectra of K9 glass measured by spectroscopy mode with 20 ns delay, 100 μs delay and 1 ms delay, respectively. The ICCD gate width was set as 1 μs. (d) Transient fluorescence signal at 580 nm measured by single-wavelength mode

Table 1. Fitting parameters of the decay curves in Fig. 3(a)

Probe(nm)	450	500	550	600
t_1 (ms)	1.34	1.38	1.01	1.42
A_1	0.28	0.31	0.32	0.32
t_2 (ms)	23.2	20.7	19.8	21.2
A_2	0.49	0.45	0.44	0.41

According to the transient absorption spectra and decay properties shown in Fig. 2 and Fig. 3, it is reasonable to suggest that two main transients could be produced with 355 nm UV laser irradiation due to the prominent absorption feature at ~450 nm (2.76 eV) and ~600 nm (2.07 eV). It should be noted that there might be other UV-induced defects in K9 glass for the complex constituents and glass network structure. However, due to the broadening of absorption bands, it is difficult to identify the other defects. Previous study has shown that irradiation induced absorption bands in visible region are always contributed to hole centers [24,25].

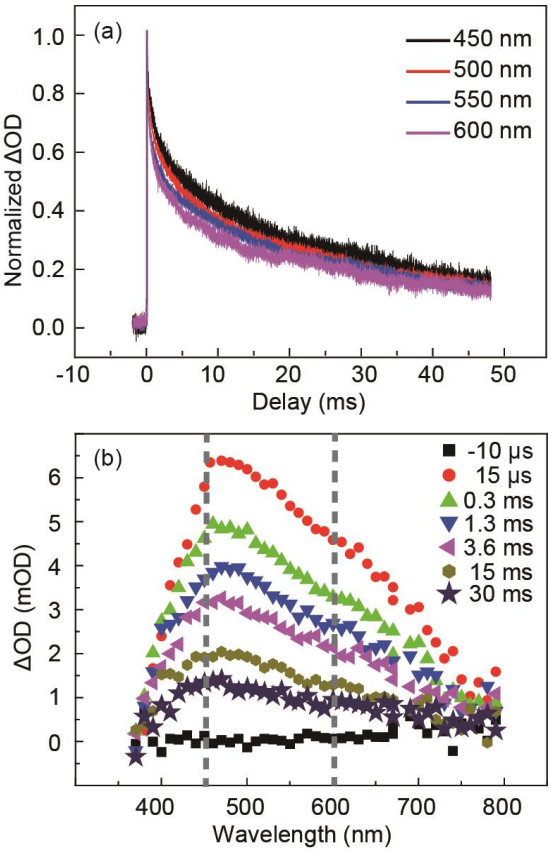

Fig. 3. (a) Temporal decay properties of laser-induced transient absorption at different probe wavelength. (b) Derived transient absorption spectra from the decay curves at different decay time. The absorption features at ~450 nm and ~600 nm are marked with dashed lines

The observed transient absorption bands at 450 nm (2.76 eV) and 600 nm (2.07 eV) mainly arise from the trapped hole centers after UV laser excitation. For alkali borosilicate glass such as K9, borate and silicate can only be mixed to a certain extent, not completely. From this point of view, there is a phase separation between the borate phase and the silicate phase in borosilicate glass at micro-scale. Thus, the as-known hole centers in borate or in silicate can be induced to coexist in K9 glass. In alkali borate glass, a prevalent hole center defect is boron oxygen hole center (BOHC) [15,26]. There are two variants of BOHC referred as $BOHC_1$ and $BOHC_2$, exhibiting absorption bands at 3.8 eV and 2.6 eV, respectively [27]. In our experiment, the observed transient absorption band at 2.76 eV can be linked to $BOHC_2$. The slight energy difference of absorption band is considered to arise from the complex local environment of the trapped hole center in borosilicate glass. Among the known defects in borate glass, there is no kind of defect correspond to absorb at 2.07 eV. So the remaining transient absorption band around 2.07 eV is related to UV-induced defect in silicate structure. In silicate glass, the 2.07 eV band is often related to the formation of non-bridge oxygen hole center (NBOHC, ≡Si-O•) during laser irradiation [28]. For alkali borosilicate glass, UV laser irradiation could break the R-O bond (R=Si or B), producing NBOHC accompany with E' center for charge conservation.

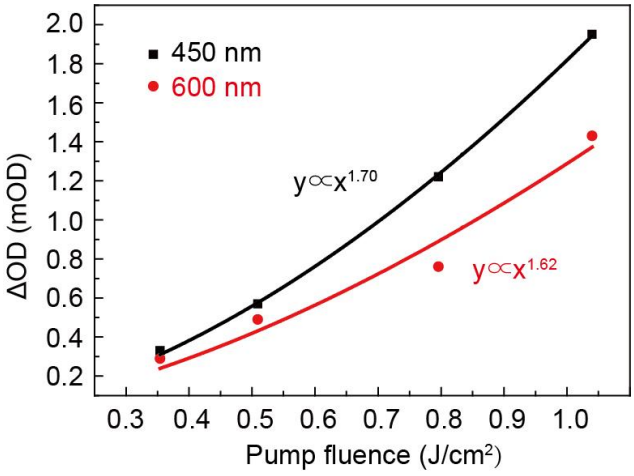

Fig. 4 Pump fluence dependency of transient absorption intensity at 450 nm (marked as "■") and 600 nm (marked as "●")

We also examined transient absorption intensity at 450 nm and 600 nm with different pump fluence, respectively. Fig. 4 shows the relationship between pump fluence and transient absorption intensity measured about 40 μs after pulsed laser excitation. The fitted pump fluence dependency of transient absorption intensity reveals a nonlinear behavior with a power-law exponent of 1.7 at 450 nm and 1.62 at 600 nm, respectively. It indicates that two or multi-photon absorption of 355 nm laser is involved to generate the structural defects described before. In K9 glass, two-photon absorption of 355 nm laser can excite electrons from the valence band to the conduction band [29]. The energetic excited electron will interact with the glass network to break the covalent bond and generate absorbing defects such as the observed trapped holes as BOHC and NBOHC. It should be noted that the UV-induced color centers are not permanent and are always metastable at room temperature. Recombination of the trapped holes by photon or thermal excited electrons would release the color centers and make the transient absorption intensity decay with time [20]. In K9 glass, it may take a relative long time for an excited electron to migrate a distance to meet a trapped hole [29]. As shown in Fig. 3, decay of the transient absorption takes several milliseconds or even longer. Such a long decay time is also a possible cause of the degeneration and fatigue effect in optics under repeated laser pulse irradiation.

4. Conclusion

In this paper, we have investigated dynamic processes of UV-laser induced hole centers in K9 glass. Our result shows that two kinds of structural defects can be produced during 355 nm laser irradiation with absorption band at 2.76 eV and 2.07 eV. They are identified as hole centers in borosilicate glass: boron oxygen hole centers (BOHC) and non-bridge oxygen hole centers (NBOHC). Both of the two defects decay at time scale of several milliseconds. We also investigated the generation mechanism of the observed hole centers, revealing that two-photon absorption of the pump laser plays an important role. The presented transient absorption study provides a feasible method to explore the defect dynamics during laser-induced damage event of optical materials.

Acknowledgments

We would like to thank Prof. L. M. Fu for providing helpful technical support and discussion. This work was supported by Development Foundation of China Academy of Engineering Physics (2013A0302016).

References

[1] R. M. Wood, Laser-induced damage of optical materials, IOP Publishing, London (2003).

[2] S. C. Jones, P. Braunlich, R. T. Casper, X. A. Shen, P. Kelly, Opt. Eng. **28**, 1039 (1989).

[3] H. J. Liu, F. R. Wang, Z. Zhang, J. Huang, X. D. Zhou, X. D. Jiang, W. D. Wu, W. G. Zheng, Proc. of SPIE **8206**, 82060T (2012).

[4] X. Wang, H. Li, J. S. Nie, Chinese J. Lasers **35**, 1760 (2008).
[5] Y. X. Pan, Z. H. Shen, J. Lu, X. W. Ni, Proc. of SPIE **8603**, 860308 (2013).
[6] H. J. Liu, J. Huang, F. R. Wang, X. D. Zhou, X. Ye, X. Y. Zhou, L. X. Sun, X. D. Jiang, Z. Sui, W. G. Zheng, Opt. Express **21**, 12206 (2013).
[7] S. G. Semos, M. Staggs, Appl. Opt. **41**, 1977 (2002).
[8] P. DeMange, R. A. Negres, C. W. Carr, H. B. Radousky, S. G. Demos, Opt. Express **14**, 5313 (2006).
[9] X. Gao, G.. Y. Feng, J. H. Han, L. L. Zhai, Opt. Express **20**, 22095 (2012).
[10] D. C. Guo, X. D. Jiang, J. Huang, F. R. Wang, H. J. Liu, X. Xiang, G. X. Yang, W. G. Zheng, X. T. Zu, Opt. Express **22**, 29020 (2014).
[11] S. O. Kucheyey, S. G. Demos, Appl. Phys. Lett. **82**, 3230 (2003).
[12] M. A. Stevens-Kalceff, A. Stesmans, J. Wong, Appl. Phys. Lett. **80**, 758 (2002).
[13] F. H. ElBatal, M. S. Selim, S. Y. Marzouk, M. A. Azooz, Physica B **398**, 126 (2007).
[14] U. Natura, T. Feurer, D. Ehrt, Nucl. Instr. and Meth. in Phys. Res. B **166-167,** 470 (2000).
[15] D. L. Griscom, Jr. G. H. Sigel, R. J. Ginther, J. Appl. Phys. **47**, 960 (1976).
[16] T. S. Wang, B. H. Duan, F. Tian, H. B. Peng, L. Chen, L. M. Zhang, W. Yuan, Chin. Phys. B **24**, 076102 (2015).
[17] E. Janata, Chem. Phys. Lett. **417**, 170 (2006).
[18] I. N. Ogorodnikov, M. S. Kiseleva, V. Y. Yakovlev, Opt. Mater. **34**, 2030 (2012).
[19] U. Schmidhammer, A. K. E. Omar, A. Balcerzyk, M. Mostafavi, Radiat. Phys. Chem. **81**, 1715 (2012).
[20] C. D. Marshall, S. A. Payne, M. A. Henesian, J. A. Speth, H. T. Powell, J. Opt. Soc. Am. B **11**, 774 (1994).
[21] C. M. Smith, N. F. Borrelli, R. J. Araujo, Appl. Opt. **39**, 5778 (2000).
[22] Z. Zhang, J. Huang, F. Geng, X. Y. Zhou, S. Q. Feng, X. L. Cheng, X. D. Jiang, W. D. Wu, W. G. Zheng, Y. J. Tang, Nucl. Instr. and Meth. In Phys. Res. B **318**, 219 (2014).
[23] M. Watanabe, S. Juodkazis, H. B. Sun, S. Matsuo, H. Misawa, Phys. Rev. B **60**, 9959 (1999).
[24] A. Bishay, J. Non-Cryst. Solids **3**, 54 (1970).
[25] E. J. Friebele, Optical Properties of Glass, American Ceramic Society, Westerville (1991).
[26] I. A. Shkrob, V. F. Tarasov, J. Chem. Phys. **113**, 10723 (2000).
[27] I. A. Shkrob, B. M. Tadjikov, A. D. Trifunac, J. Non-Cryst. Solids **262**, 6 (2000).
[28] L. Skuja, J. Non-Cryst. Solids **239**, 16 (1998).
[29] J. J. Adams, T. McCarville, J. Bruere, J. McElroy, J. Peterson, Proc. of SPIE **5273**, 177 (2003).

*Corresponding author: frwang2006@sina.com