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Laser-induced incandescence of borate glass doped with carbon microparticles

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A method of synthesis of alkali-borate glass activated with carbon microparticles is proposed. The behavior of thermal emission of carbon microparticles in the glass under excitation by a *Q*-switched neodymium laser is investigated. With the increase of laser irradiation dose, the fading of laser-induced emission observed in experiment is interpreted to be due to the carbon particle size reduction caused by the laser irradiation.

Предложен метод синтеза щелочно-боратных стекол, активированных микрочастичками углерода. Исследованы закономерности теплового свечения микрочастичек углерода в стекле при возбуждении излучением неодимового лазера с модуляцией добротности. Экспериментально наблюдаемое выгорание свечения стекла объяснено уменьшением размера частичек углерода вследствие лазерного облучения.

1. Introduction

Fine-dispersed materials comprising the light-absorbing microparticles in transparent matrices draw attention of researchers for their unusual properties under high-power pulsed laser irradiation. Carbon suspensions, inks, carbon black particles formed in the air as a result of organic fuel combustion, turbid natural water, etc. are typical examples. In such objects, with the use of nanosecond-scale laser pulses, laser-induced heating of microparticles to a temperature of a few thousand degrees is observed at 10 to 100 MW/cm^2 laser power. Thermal emission of such media under pulsed laser excitation is observed to a naked eye and is called laser-induced incandescence (LII) [1–6]. In transparent liquid matrices with suspended light-absorbing microparticles, microbubbles are produced near the laser-heated microparticles together with LII. Those microbubbles are formed due to the vaporization of particles and surrounding liquid, to chemical interaction of heated microparticle material with liquid, to the pyrolysis of organic matrix, etc. The laser-induced microbubbles cause significant increase of light scattering in the irradiated suspension, hence its optical transmittance changes. As far as microbubbles have time to grow during the leading edge of the laser pulse, self-induced attenuation of high-power pulsed laser radiation (optical limiting phenomenon) is observed in such suspensions [6–9]. The phenomenon of optical limiting by the mechanism of laser-induced enhancement of light scattering makes it possible to develop passive devices for protection of eyes and optical instruments against accidental damage with high-power laser radiation within a wide spectral range.

Investigation of interaction of high-power laser radiation with fine-dispersed light-absorbing materials is not only of applied interest. Physical processes which occur around the laser-heated microparticle are complex and diverse. Such research extends our knowledge on the processes of

light-matter interaction and serve as a background for the development of methods for controlling optical properties of materials using high-power laser radiation.

In this work, we investigate oxide (borate) glass doped with carbon microparticles under high-power excitation by *Q*-switched neodymium laser radiation. The glass matrices activated by light-absorbing microparticles are poorly investigated under high-power laser excitation, substantially due to the deficiency of such objects. For example, observation of laser-induced incandescence of borate glass containing microparticles of unknown nature was first reported in [10]. In the current study, we proceed with the investigation of LII in oxide glass with the use of specially synthesized glass activated by carbon microparticles.

2. Experimental details

For preparation of LII-capable glass samples, a synthesis method was developed for the alkali-borate glass activated with carbon microparticles. Carbon microparticles were embedded into sodium-borate glasses with various content of alkaline oxide: $Na_2O{\cdot}2B_2O_3$, $Na_2O{\cdot}4B_2O_3$, and $Na_2O{\cdot}7B_2O_3$. The boron oxide B_2O_3, sodium carbonate Na_2CO_3 and activated carbon (approximately 2 wt.%) were used as ingredients. The carbon was used in the charge as a powder with particle size not more than 0.1 mm. The glass synthesis was carried in air at 1000°C in a quartz crucible during 1.5 h. During the glass synthesis, due to the convective agitation of the glass, some of the carbon particles were carried to the surface of the glass bath, hence the bright flashes were observed at the melt surface. After 1.5 h of soaking in the furnace, the melt was poured into the preheated aluminum molds and the obtained samples were annealed at 350°F255C during 10 h. As a result, glass samples were obtained, without visible signs of carbon particles inside. The remainder of the largest carbon particles was observed at the bottom of the crucible. Nevertheless, the presence of carbon microparticles in the glass samples was confirmed by scattering of probe laser light and by the LII experiments under high-power laser excitation. Undoped glasses prepared in similar conditions (without addition of carbon to the charge) did not demonstrate LII.

Note should be made that the obtained samples of $Na_2O{\cdot}2B_2O_3$ glass differ essentially from the samples with lower content of the oxide-modifier ($Na_2O{\cdot}4B_2O_3$ and $Na_2O{\cdot}7B_2O_3$). The samples of $Na_2O{\cdot}2B_2O_3$ glass did not demonstrate LII under high-power infrared laser excitation, because all of the carbon added to the charge burns away in the process of glass synthesis. As is known, the viscosity of melted alkali-borate glass with high content of oxide-modifier is approximately four times lower that the viscosity of low-alkaline glass at the same temperature [11]. During the glass synthesis, convective agitation is much more intense in $Na_2O{\cdot}2B_2O_3$ glass, hence in these samples practically all carbon is burned out due to the interaction with air at the surface of glass melt. Besides, after finishing of the synthesis, the remainder on the bottom of the crucible with $Na_2O{\cdot}2B_2O_3$ glass does not contain carbon particles. The attempts to prepare $Na_2O{\cdot}2B_2O_3$ glass samples doped with carbon microparticles by shortening the synthesis time failed because the obtained samples were mechanically unstable and quickly broke down. Thus, in this work we used for experiments $Na_2O{\cdot}4B_2O_3$ and $Na_2O{\cdot}7B_2O_3$ glass samples activated with carbon microparticles. The particle size was difficult to measure, because the obtained glass samples were not homogeneous enough to be suitable for nephelometric measurements. Besides, the attempts to measure the particle size in the glass samples using an optical microscope also failed.

In the experiments, a *Q*-switched YAG:Nd^{3+} laser was employed (wavelength 1064 nm, 25 ns pulse duration, power density 20–100 MW/cm^2, laser pulse repetition cycle 0.5–2 s). Laser irradiation of the glass samples was combined with the measurement of the LII intensity. All measurements were performed at room temperature. The glass samples satisfied the conditions of optically thin layer (optical density much below a unit).

Under pulsed laser excitation, the observed LII emission was also pulsed, with typical duration of 30 to 50 ns. The LII intensity was detected by a photomultiplier at a fixed wavelength. The signal from the photomultiplier was integrated; hence the energy of LII pulse was measured. For oscillographic measurements of LII pulse shape, a nanosecond-resolution photomultiplier 14ELU-FS was employed together with an oscillograph 6LOR-04 operating in the single-pulse mode.

3. Results and discussion

Under high-power infrared laser excitation, all samples of $Na_2O{\cdot}4B_2O_3$ and $Na_2O{\cdot}7B_2O_3$ glasses doped with carbon microparticles demonstrate clearly detectable white emission in the whole visible spectral range. The pulse duration of this emission is approximately two times longer than that of the laser pulse. In non-activated glass samples, laser-induced white emission is several orders of magnitude less intense than in doped samples.

Phenomenological characteristics of the observed white emission of carbon-doped glass samples under high-power laser excitation argue for the thermal mechanism of its origin, similarly to LII in aqueous carbon suspensions [4]. Thus, the incandescence of glass has a wide structureless spectrum which covers all the visible area. The intensity of incandescence, I_{LII}, depends on the laser excitation intensity, F, essentially nonlinearly. The nonlinearity factor $\gamma = dI_{LII}/I_{LII}/dF/F$ takes a range of values $\gamma = 2...4$ typical for Planck's thermal emission at a fixed wavelength in the visible spectral range [4]. The nonlinearity factor γ is not constant and decreases with the increase of laser excitation intensity. Such behavior of γ with is also a typical feature of LII emission.

For glass samples doped with carbon microparticles, the experiments show that the LII intensity depends on the dose of irradiation with a sequence of laser pulses. We define the dose of irradiation, N, as a number of laser pulses in a sequence which irradiates the same volume of the glass sample. The dependence of LII intensity at a fixed wavelength (500 nm) on the dose of laser irradiation is shown in Fig. 1 for $Na_2O{\cdot}4B_2O_3$ glass doped with carbon microparticles. A similar behavior is observed with $Na_2O{\cdot}7B_2O_3$. The measurements were carried out at two values of the laser power density: 20 MW/cm^2 (Fig. 1, curve *1*) and 100 MW/cm^2 (Fig. 1, curve *2*).

As is seen from Fig. 1, major decrease of the LII intensity (LII fading) with laser irradiation dose is observed during the first dozen of laser pulses, whereas subsequent pulses practically do not affect the LII intensity Fig. 1 also shows that the relative decrease of the LII intensity with the laser irradiation dose depends on the power density of the laser radiation. A fivefold increase of the laser power density leads to approximately the same (fivefold) enhancement of the LII fading effect.

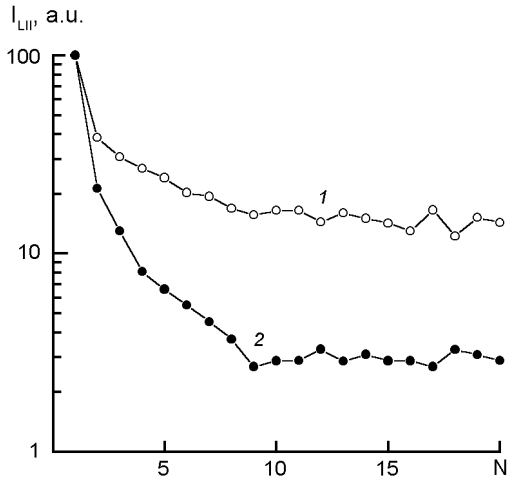

Fig. 1. The dependences of LII intensity at 500 nm on the dose of laser irradiation with power density of 20 (curve *1*) and 100 MW/cm^2 (curve *2*) for $Na_2O{\cdot}4B_2O_3$ glass doped with carbon microparticles.

The observed dose dependence of LII intensity (Fig. 1) can be explained with the following considerations. As is known for carbon black suspensions, the temperature of laser-heated carbon microparticles can exceed 4000 K, at which carbon evaporates, hence the particle dimensions decrease with the increase of laser irradiation dose [12]. The mentioned decrease of particle size in laser-irradiated carbon suspensions manifests itself in various experiments. For example, laser irradiation causes LII intensity fading, LII pulse shortening, and significant changes in the light scattering indicatrix [13]. Concerning the observed LII fading in carbon-doped glass, it is plausible to suggest that laser-induced overheating of carbon microparticles and of neighboring glass layers results in a significant enhancement of carbon transfer from the microparticle to the surrounding glass, for example, into the voids of the glass oxide network. As a result, the glass changes its properties in the vicinity of a carbon microparticle, and the carbon core decreases in size, which leads to the decrease of LII intensity under laser irradiation.

As is seen from Fig. 1, the rate of LII intensity fading with the laser irradiation dose strongly decreases after a few laser pulses. This fact can be explained by the following considerations. The laser irradiation changes the properties of the glass around the carbon microparticles. These

changes can be caused by the enhancement of carbon transfer, partial melting of the glass and its fast recrystallization, the appearance of mechanical stresses, etc. It is plausible to suggest that the laser-produced shells around carbon microparticles can partially absorb and scatter the laser light. This leads to the decreased effective intensity of laser excitation of carbon microparticles, hence the particles are less heated and the decrease of LII intensity with the laser irradiation dose slows down (Fig. 1).

As a confirmation of the model proposed above, the following results of the experiments can be considered. The intensity of LII at two fixed wavelengths (400 and 600 nm) was measured as a function of laser irradiation dose. The experiments show that I_{LII} at 400 nm decreases 15 % more than I_{LII} at 600 nm after irradiation with $N = 3$–5. This indicates that the laser irradiation causes a considerable red shift of the emission spectrum, which can be interpreted as the decrease of the effective particle temperature with the increase of laser irradiation dose.

We have also investigated the shape of LII pulses with the increasing laser irradiation dose. The oscillograms of LII pulses of $Na_2O{\cdot}4B_2O_3$ glass sample doped with carbon microparticles are shown in Fig. 2. Here, LII is detected in the 450–400 nm spectral region. As is seen from Fig. 2, the LII pulses become shorter with the increase of laser irradiation dose. While the duration (at 50 % level) of the first LII pulse ($N = 1$) is about 50 ns, the second and subsequent pulses are about 40 ns. Fig. 2 shows that LII decay time shortens after the laser irradiation.

The decay of LII pulse is determined by the carbon particle cooling rate. The kinetics of particle temperature decay can be described by the following approximate equation

$$c\rho\frac{4}{3}\pi R^3 dT = \qquad (1)$$
$$= -\left[k\frac{T - T_S}{\Delta r} + \sigma(T^4 - T_S^4)\right]4\pi R^2 dt,$$

where c, ρ are the specific heat and density of carbon, respectively; R, the particle radius; $(T-T_S)\Delta r^{-1}$, the temperature gradient; T_S, the surrounding matrix temperature; k, the heat conductivity factor; and σ is the Stefan-Boltzmann constant. In equation (1), it is supposed that the laser pulse is sharply

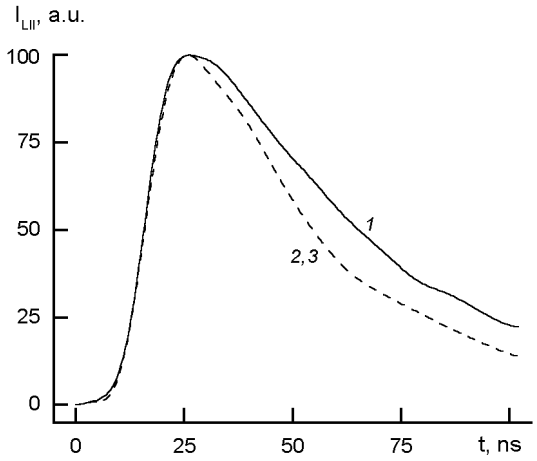

Fig. 2. The oscillograms of LII of $Na_2O{\cdot}4B_2O_3$ glass sample at 100 MW/cm^2 of laser excitation. The curves are enumerated by the number of the laser pulses in the irradiation sequence.

terminated and that thermal relaxation inside the particle is much faster than the relaxation to the environment. Besides, equation (1) does not account for the processes of particle vaporization.

For the conditions of the experiments in this work, numerical estimates show that heat emission is a negligible part in the particle energy balance. Hence, on condition $T >> T_S$, typical time of thermal relaxation can be estimated from (1) as follows

$$\tau = \frac{c\rho R\Delta r}{3k}.$$

The distance $\sqrt{D\tau}$ which thermal wave passes during the time τ can be used as an estimate of Δr, where D is the temperature conductivity of the glass. Then we get that the time of thermal relaxation is proportional to the squared particle radius

$$\tau = \left(\frac{c\rho R}{3k}\right)^2 D.$$

Thus, if the particle cooling is determined mainly by heat transfer into the environment, then the decrease of the effective particle size results in the decrease of LII decay time. From Fig. 2, it follows that typical LII decay time is about 50 ns. Numerical estimates based on the Planck's blackbody emission law show that the observed 20 % decrease of LII pulse duration can be caused by the 10 % decrease of the carbon particle effective radius.

Note should be made that the above considerations do not account for possible changes of heat transfer properties (k,D) of the neighboring glass layers. The laser-induced increase of heat conductivity coefficient of glass in the shell around the carbon core can also cause a decrease of τ.

4. Conclusions

Borate glass doped with carbon microparticles is a suitable object for observation of LII in transparent solid matrix. It is worth noting that pulsed laser heating of carbon microparticles does not cause any visible destruction of the glass samples though the local temperature reaches thousands of Kelvins. The intensity of laser-induced incandescence in borate glass depends on prehistory of the glass sample laser irradiation. The observed LII fading at the increase of laser irradiation dose is a consequence of the reconstruction of absorption/emission centers, probably due to the carbon transfer from laser-heated microparticles into the neighboring glass layers. The reconstruction includes (i) the decrease of the effective size of carbon microparticles and (ii) the changes of optical and thermal properties of the surrounding glass layers.

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Теплове випромінювання боратного скла, активованого мікрочастинками вуглецю

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Розроблено методику синтезу натрієво-боратного скла, активованого мікрочастинками вуглецю. Досліджено закономірності теплового випромінювання вуглецевих мікрочастинок у склі при збудженні випромінюванням неодимового лазера з модуляцією добротності. Вигоряння світіння скла, що спостережується експериментально, пояснене зменшенням розміру частинок вуглецю внаслідок лазерного опромінення.