

# Dissolution in a supercritical liquid as a mechanism of laser ablation of sapphire

S I Dolgaev, M E Karasev, L A Kulevskii, A V Simakin, G A Shafeev

**Abstract.** The laser ablation of sapphire is studied by irradiating its interface with water and aqueous solutions of KOH, KCl and Na<sub>2</sub>CO<sub>3</sub> by 2.92- $\mu\text{m}$  130-ns holmium laser pulses. The ablation rate depends on the concentration and type of the dissolved substance. The highest ablation rate is 2.5  $\mu\text{m}$  per pulse for a laser fluence of 120 J cm<sup>-2</sup>. The ablation of sapphire is attributed to its dissolution in water or in aqueous solutions in the supercritical state.

**Keywords:** laser ablation, sapphire, hydrothermal dissolution, supercritical liquid.

## 1. Introduction

Effective ablation of sapphire upon irradiation by 510.6-nm copper vapour laser pulses was reported in Refs [1, 2]. Ablation occurs when the sapphire interface with aqueous solutions absorbing laser radiation is irradiated by the laser through sapphire. Since sapphire and water are transparent to copper vapour laser radiation, absorbing substances are dissolved in water to increase absorption. Under the conditions used in papers [1, 2], the typical absorption coefficients were  $\sim 500 \text{ cm}^{-1}$ .

The presence of absorbing substances like CrO<sub>3</sub>, FeCl<sub>3</sub>, KMnO<sub>4</sub> dissolved in water leads to the deposition of insoluble (in water) oxide films on the sapphire surface under the action of laser radiation [3–5]. The film deposition is caused by the thermal decomposition (pyrolysis) of substances dissolved in water, which occurs at the focus of the laser beam in the immediate vicinity of the substrate. Because the laser radiation is focused on the interface of sapphire with the solution through the absorbing film, the optical thickness of the film is inversely proportional to the intensity of laser radiation [6]. The presence of an absorbing film under the conditions of multipulse laser irradiation may lead to ablation of the substrate due to a difference in the coefficients of thermal expansion of the film and the substrate [7]. A layer of the material of the substrate is destroyed and removed from the surface along with the film, i.e., ablation of the substrate takes place.

In addition to the film formation, other mechanisms participating in this process include the action of pressure wave, generated upon absorption of laser radiation in the liquid, on the sapphire surface, as well as the action of water in the supercritical state on sapphire. The supercritical state of water is characterised by a high pressure and temperature ( $p_{\text{cr}} = 22.12 \text{ MPa}$ ,  $T_{\text{cr}} = 647 \text{ K}$  [8]) at which sapphire is easily dissolved in water [9]. In the case of sapphire ablation in aqueous solutions, a combined action of the above-mentioned processes can be envisaged, however, the contribution from each mechanism to the overall ablation rate, which achieves 0.12  $\mu\text{m}$  pulse<sup>-1</sup> [1, 2], remains unknown.

To eliminate the effect of film formation on the ablation process, one should use as the liquid absorbing laser radiation either pure water or aqueous solutions whose exposure to laser radiation does not result in the deposition of insoluble films. Like other liquids containing the hydroxyl group, water is a strongly absorbing medium for optical radiation in the mid-IR range. The maximum of the absorption coefficient of water lies at  $\sim 3 \mu\text{m}$ , where its value is  $\sim 10^4 \text{ cm}^{-1}$  [10].

The action of pulsed laser radiation on the absorbing liquid is accompanied by the heating of the liquid and the generation of a pressure pulse in it [11, 12]. If the absorption coefficient of the liquid is  $\sim 10^4 \text{ cm}^{-1}$ , the region being heated by the radiation has a thickness of the order of one micrometer. The high energy deposition per pulse into the heating region during the propagation of a pulse may transform the liquid to the supercritical state. Exposure of the interface between sapphire and the absorbing liquid to laser radiation may lead to the interaction of sapphire with the liquid in the supercritical state in which the solubility of sapphire is considerably enhanced.

The aim of this paper is to study the ablation of sapphire caused by irradiation of its interface with aqueous solutions by  $\sim 3\text{-}\mu\text{m}$  laser pulses, and to determine its mechanisms.

## 2. Experimental

We used an yttrium-scandium-gallium-garnet laser (YSGG:Cr<sup>3+</sup>:Yb<sup>3+</sup>:Ho<sup>3+</sup>, the <sup>5</sup>I<sub>6</sub>–<sup>5</sup>I<sub>7</sub> transition of Ho<sup>3+</sup> ions) emitting at 2.92  $\mu\text{m}$  as the radiation source. The absorption coefficient of water at this wavelength is  $\alpha \approx 1.3 \times 10^4 \text{ cm}^{-1}$  [10]. Q-switching was produced using a LiNbO<sub>3</sub> switch [13]. The pulse energy was  $\sim 10 \text{ mJ}$ , the pulse repetition rate was  $f = 1 \text{ Hz}$ , and a pulse duration was 130 ns. The radiation was focused by a fluorite lens of focal length 10 cm to a spot of diameter  $\sim 100 \mu\text{m}$  (by the 1/e level), so that the energy density at the focus of the laser beam was  $\sim 120 \text{ J cm}^{-2}$ . A number of experiments were

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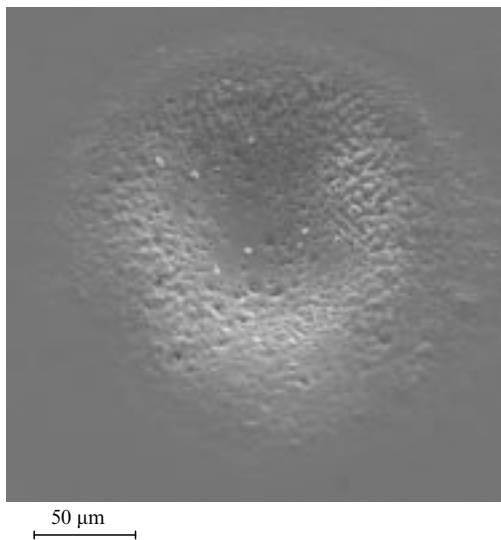
made using a 2.94- $\mu\text{m}$  free-running  $\text{Er}^{3+}$ :YAG laser with a pulse energy of  $\sim 0.5$  J and a pulse duration of 150  $\mu\text{s}$ . The energy density at the focus of the laser beam achieved  $500$   $\text{J cm}^{-2}$ .

Plane-parallel sapphire substrates were glued to the side of the cell exposed to laser radiation in the experiments. The laser radiation was focused on the sapphire-liquid interface through the sapphire substrate. Aqueous solutions of KOH, KCl and  $\text{Na}_2\text{CO}_3$  of different concentrations, as well as pure water, were used as the absorbing media for laser radiation. It was assumed that the absorption coefficients  $\alpha$  of aqueous solutions at the laser radiation wavelength did not differ significantly from the absorption coefficient for pure water and were  $\sim 10^4$   $\text{cm}^{-1}$ . For example, the absorption coefficient of water and the aqueous solutions of KOH with concentrations 4 and 8  $\text{mol litre}^{-1}$ , calculated from the data presented in Ref. [10], were  $1.24 \times 10^4$ ,  $1.03 \times 10^4$ , and  $0.82 \times 10^4$   $\text{cm}^{-1}$ , respectively. No ablation of sapphire was observed in the absence of the aqueous medium for the same values of the laser radiation parameters.

After exposure to laser radiation, the sapphire surface was viewed through a scanning electron microscope as well as an optical microscope.

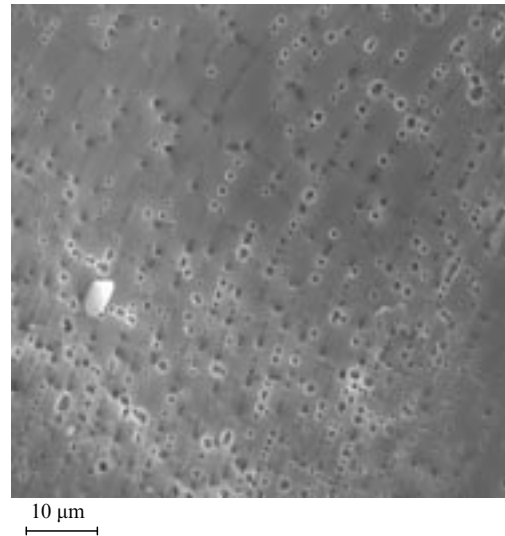
### 3. Experimental results

Exposure of the sapphire-aqueous solution interface to several laser pulses results in the formation of an indentation at its surface with a diameter close to the diameter of the focused laser beam (Fig. 1), the depth of the indentation increasing with the number of laser pulses. Upon further irradiation, the indentation develops into a channel directed along the laser beam axis. The shape of the indentations depends neither on the matter dissolved in water nor on its concentration. The surface of indentations is covered by pits of micrometer size (Fig. 2).

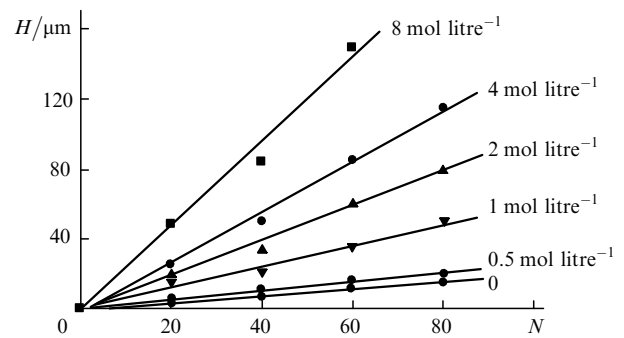


**Figure 1.** Indentation formed in sapphire after irradiation of the interface between sapphire and aqueous solution of  $\text{Na}_2\text{CO}_3$  with a concentration  $2$   $\text{mol litre}^{-1}$  by 20 laser pulses of fluence  $120$   $\text{J cm}^{-2}$ .

A linear growth in the depth of the channels with the number of laser pulses was observed in all the aqueous solutions used in our experiments. Fig. 3 shows the corre-

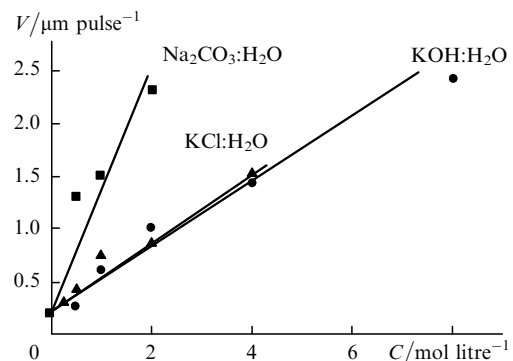


**Figure 2.** A typical view of the pits formed at the bottom of an indentation.



**Figure 3.** Dependences of the depth  $H$  of channels formed in sapphire on the number  $N$  of laser pulses irradiating the interface between sapphire and aqueous solution of KOH. The numbers indicate the concentration of KOH in the solution. The fluence at the focus of the laser beam is  $120$   $\text{J cm}^{-2}$ .

sponding dependences for an aqueous solution of KOH. The dependences of the channel depth growth rate (ablation rate) in sapphire on the concentration of aqueous solutions of KOH, KCl, and  $\text{Na}_2\text{CO}_3$  are shown in Fig. 4. One can



**Figure 4.** Dependences of the sapphire ablation rate  $V$  on concentration  $C$  of the substance dissolved in water. The ablation rate of sapphire in pure water is  $0.24$   $\mu\text{m pulse}^{-1}$ .

see that despite a certain decrease in the absorption coefficient of the solution, the ablation rate increases with the concentration of the dissolved substance. The ablation rate of sapphire in the aqueous solutions of KOH and KCl are almost identical, i.e., the observed ablation rate is only determined by the type of cations in the solution. The rate of increase in the channel depth is an order of magnitude higher than that in pure water, which is about of  $0.2 \mu\text{m pulse}^{-1}$  under the same conditions. The highest ablation rate observed in our experiments was  $2.5 \mu\text{m pulse}^{-1}$  for an energy density of  $120 \text{ J cm}^{-2}$  and the KOH concentration of  $8 \text{ mol litre}^{-1}$ .

For the case of an Er laser with a pulse duration of about  $150 \mu\text{s}$ , ablation of sapphire was not observed up to the energy densities of  $500 \text{ J cm}^{-2}$  under the same irradiation conditions.

#### 4. Discussion

When a sapphire–aqueous solution interface is irradiated by a laser pulse, a region of high pressure and high temperature is formed adjacent to the sapphire surface at the focus of the laser beam. The amplitude of the pressure pulse may be as high as several kilobars and exceed the critical pressure [12], while the temperature of the liquid may be much higher than the critical value in spite of the fact that the critical point in solutions is displaced towards higher pressures and temperatures as compared to the pure solvent. Unfortunately, the pressure and temperature produced in the liquid cannot be calculated because the interaction of intense laser radiation with the liquid is not in equilibrium and is accompanied by a change in the aggregate state.

Under normal conditions, a sapphire crystal is difficultly soluble in water. However, it is known that the solubility of sapphire, as of many other crystals, increases significantly with pressure and temperature (the so-called hydrothermal dissolution conditions [9]). This is due to a replacement of  $\text{Al}^{3+}$  ions in the crystal lattice of sapphire by the ions contained in the aqueous solution. The dissolution process is most efficient in alkaline aqueous solutions of NaOH, KOH,  $\text{Na}_2\text{CO}_3$  at temperatures above  $400^\circ\text{C}$  and under pressures of several kilobars [14]. For example, the solubility of sapphire at a temperature of  $500^\circ\text{C}$  and under a pressure of 2 kbar achieves 40 g per 100 ml of the aqueous solution of  $\text{Na}_2\text{CO}_3$  [15], while its solubility in water under normal conditions is  $9.8 \times 10^{-5}$  g per 100 ml [9]. Therefore, we can expect that under the conditions of our experiments, sapphire will be efficiently dissolved in the region irradiated by a laser beam.

This assumption is confirmed by the morphology of the ablation region. The dissolution of crystals is usually accompanied by the formation of etch or dissolution pits on their surface [16]. Such pits of about 1 micrometer size are observed on the sample surface in the region irradiated by a laser beam (see Fig. 2). The ordered arrangement of pits may be due to the emergence of crystal lattice defects on the sample surface, which are pushed to the sapphire surface by the pressure wave.

The dependence of the ablation rate for sapphire on the type of ions in the solution also confirms the assumption concerning the predominant contribution of the dissolution of sapphire to ablation. In particular, it follows from Fig. 4 that the ablation rate in aqueous solutions containing  $\text{Na}^+$

ions is higher than in solutions containing  $\text{K}^+$  ions for identical ionic concentrations. At the same time, one can see that the sapphire ablation rates for the aqueous solutions of KOH and KCl are almost identical, which leads to the assumption that the dissolution rate is determined by the concentration and type of cations and is almost independent of the concentration and type of anions in the solution. This is a characteristic feature of the hydrothermal dissolution of sapphire, as also the order-of-magnitude increase in its dissolution rate upon the addition of alkali metal ions into solution, as compared to its dissolution rate in pure water [15].

Upon irradiation of a sapphire by a laser pulse, a pressure wave with an amplitude of several kilobars is generated on the side of the liquid, which may lead to the formation of crystal structure defects and microcracks on its surface. In the multipulse regime of irradiation of the interface between the media, the defect-saturated sapphire surface is subjected to the action of the liquid in the supercritical state upon irradiation by subsequent laser pulses. Therefore, a pressure wave with a large amplitude may also contribute to the sapphire ablation.

A significant distinction between sapphire dissolution upon laser irradiation of its interface with the absorbing liquids and its dissolution under equilibrium hydrothermal conditions is a strong nonuniformity of the temperature distribution at the interface between the two media. According to simulations of the temperature distribution during pulsed laser heating of the sapphire interface with a liquid [5], the maximum of the temperature distribution lies inside the liquid, while the sapphire itself remains virtually cold. Such a temperature distribution is caused by a large difference in the thermal conductivities of the two media ( $k_1/k_2 \sim 70$ ). The effect of this peculiarity of the temperature distribution on the solubility of sapphire requires further investigation.

The possibility of emergence of conditions for hydrothermal dissolution of sapphire depends on the rate of energy deposition in the medium. For slow deposition of energy, the pressure and temperature of the aqueous medium do not probably achieve values large enough for a rapid dissolution of sapphire. Indeed, no ablation of sapphire irradiated by an  $150\text{-}\mu\text{s}$  erbium laser pulses with a intensity of  $3 \times 10^6 \text{ W cm}^{-2}$  was observed even after exposure to several hundred laser pulses, in contrast to irradiation by  $130\text{-ns}$   $10^9\text{-W cm}^{-2}$  holmium laser pulses, the absorption coefficients for the laser radiation in the liquid being the same in both cases.

Thus, it is shown in this work that the dissolution of sapphire may be one of the mechanisms of ablation upon irradiation of its interface with absorbing aqueous solutions. Note that dissolution also plays a significant role in the case of laser ablation of sapphire produced by a copper vapour laser [1, 2]. This conclusion is based on the fact that the rate of sapphire ablation in this case is of the same order of magnitude as upon irradiation by a holmium laser.

#### 5. Conclusions

Let us call attention to the possible practical applications of the process studied in this work. The use of sapphire, which possesses a high hardness and chemical stability, as a material for construction is hampered by the absence of methods for its processing. The process of laser ablation

considered in this work makes it possible to drill through holes in sapphire and to shape its surface in accordance with a preset drawing, for example, for the manufacturing of dies for the production of fibres. Thus, laser-induced dissolution of sapphire is certainly of technological interest.

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## References

1. Dolgaev S I, Lyalin A A, Simakin A V, Shafeev G A *Kvantovaya Elektron.* **23** 67 (1996) [*Quantum Electron.* **26** 65 (1996)]
2. Dolgaev S I, Lyalin A A, Simakin A V, Shafeev G A *Appl. Surface Science* **96-98** 491 (1996)
3. Voronov V V, Dolgaev S I, Shafeev G A *Dokl. Akad. Nauk* **358** 465 (1998)
4. Dolgaev S I, Voronov V V, Shafeev G A *Appl. Phys. A* **66** 87 (1998)
5. Dolgaev S I, Kirichenko N A, Shafeev G A *Appl. Surface Science* **138-139** 449 (1999)
6. Simakin A V, Lubnin E N, Shafeev G A *Kvantovaya Elektron.* **30** 263 (2000) [*Quantum Electron.* **30** 263 (2000)]
7. Simakin A V, Lubnin E N, Shafeev G A *Appl. Phys. A* **69** 267 (1999)
8. Grigor'ev I S, Meilikhov E Z (Eds.) *Fizicheskie Velichiny. Spravochnik* (Handbook of Physical Quantities) (Moscow: Energoatomizdat, 1991)
9. Belyaev L M (Ed.) *Rubin i Saffir* (Ruby and Sapphire), (Moscow: Nauka, 1974)
10. Zolotarev V M, Morozov V N, Smirnova E V *Opticheskie Postoyannye Prirodnykh i Tekhnicheskikh Sred. Spravochnik* (Optical Constants of Natural and Artificial Media. A Handbook) (Leningrad: Khimiya, 1964)
11. Bunkin F V, Karlov N V, Komissarov V M, Kuz'min G P *Pis'ma Zh. Eksp. Teor. Fiz.* **13** 479 (1971)
12. Bunkin F V, Tribel'skii M I *Usp. Fiz. Nauk* **130** 193 (1980)
13. Zavartsev Yu D, Zagumennyi A I, Kulevskii L A, et al. *Kvantovaya Elektron.* **27** 13 (1999) [*Quantum Electron.* **29** 295 (1999)]
14. Chernov A A, Givargizov E I, Bagdasarova Kh S, et al. *Sovremennaya Kristallografiya T. 3. Obrazovanie Kristallov* (Modern Crystallography. Formation of Crystals) (Moscow: Nauka, 1980), vol. 3.
15. Lobachev A N (Ed.) *Gidrotermal'nyi Sintez Kristallov* (Hydrothermal Synthesis of Crystals) (Moscow: Nauka, 1968)
16. Sangwal K *Etching of Crystals. Theory, Experiment and Application* (Elsevier Science Publishers, Netherlands, 1987; Moscow: Mir, 1990)