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Nonlinear absorption in optical materials at a wavelength of 193 nm

M.Yu. Artem'ev, V.M. Nesterov, A.P. Sergeev, P.B. Sergeev

***Abstract*. The coefficients of two-photon absorption of 30- and 70-ns ArF laser pulses in high-purity CaF_2, BaF_2, and Al_2O_3 crystals are measured by the method of nonlinear transmission to be 2.2 ± 0.8, 2.3 ± 0.8, and 5.6 ± 2.2 cm GW^{-1}, respectively. The thresholds of the laser breakdown of the surface of crystals are determined.**

Keywords: *optical materials, UV laser radiation, nonlinear absorption.*

1. Introduction

The energy of a photon emitted by an ArF laser at a wavelength of 193 nm is equal to 6.4 eV. Because this energy exceeds half the energy gap width for almost any optical material, two-photon absorption of this radiation dominates among processes of the interaction of laser radiation with optical materials. The understanding of these processes is necessary for evaluating the outlook for the ArF laser and other short-wavelength VUV lasers.

The ArF lasers usually emit 10 – 100-ns pulses. The coefficient of two-photon absorption of such pulses in optical materials is, as a rule, substantially greater than that for picosecond pulses. This is explained by the additional absorption of laser radiation by short-lived electronic states of optical materials, which have time to form during the recombination of electron – hole pairs generated due to classical two-photon ionisation [1, 2]. The experimental measurements of two-photon absorption coefficients β of optical materials at different pulse durations τ and different wavelengths λ play a key role in the development of theoretical models of these processes for UV and VUV laser radiation. This makes the measurement of these absorption coefficients under different conditions the topical problem.

The aim of this paper is to measure the value of β for high-purity CaF_2, BaF_2, and Al_2O_3 crystals irradiated by 193-nm, 30- and 70-ns pulses. High-purity fluorite attracts considerable attention of researchers because of its high stability to UV and VUV laser radiation [3 – 6]. The nonlinear absorption of the 193-nm radiation in this material was studied in Refs [7 – 10]; however the results are insufficient, especially for obtaining the dependence $\beta(\tau)$ [10]. We have earlier failed to measure β for the BaF_2 and leucosapphire crystals irradiated by 70-ns pulses because of a low radiation resistance of their surface [11]. Such measurements proved to be possible with new samples irradiated by 30-ns pulses.

2. Experimental

We measured two-photon absorption coefficients β of crystals by the standard method of nonlinear transmission [12, 13] using an electric-discharge ArF laser emitting 250-mJ, 30-ns pulses (Fig. 1a). The variation in the pulse energy E from pulse to pulse did not exceed 10 % of the average value. The pulse repetition period was approximately 3 min. The cross-sectional area of the laser output beam was 2×1 cm. The laser beam was divided with a beam-splitter into two beams. One of the beams was incident on an IMO-2 calorimeter to control the laser energy in each pulse. The second beam was focused with a KU1 quartz lens on a sample, behind which a second IMO-2 calorimeter

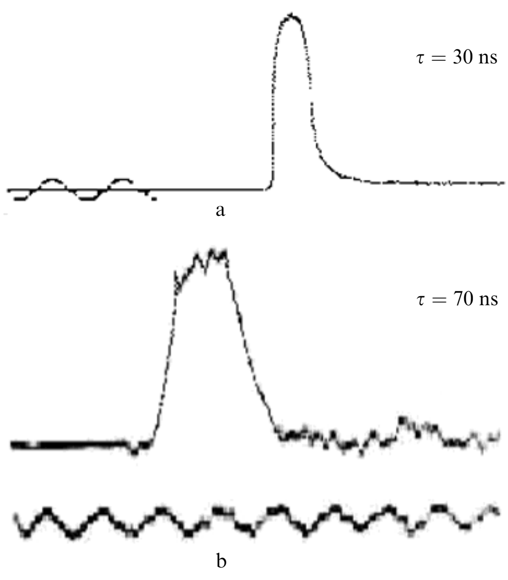

Figure 1. Shapes of pulses from the electric-discharge (a) and e-beam-pumped (b) ArF lasers. The sine curve with a period of 50 ns shows time marks.

M.Yu. Artem'ev, V.M. Nesterov, A.P. Sergeev, P.B. Sergeev P.N. Lebedev Physics Institute, Russian Academy of Sciences, Leninskii prosp. 53, 119991 Moscow, Russia

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was placed to measure the laser energy transmitted through the measuring path.

Most of the experiments were performed using a KU1 quartz lens with the focal distance 111 cm. First, we measured the divergence θ of laser radiation with the help of apertures placed in the focal plane. The values of θ_1 and θ_2 measured in two mutually perpendicular directions at the 0.65 level of the total energy E were 6×10^{-4} and 4×10^{-3} rad, respectively. The area S of the focal spot, in which up to 65 % of the total energy was concentrated, was 3 mm^2. The caustic length in the beam cross section in the direction of a lower divergence exceeded 3 cm. The maximum intensity I of laser radiation in the caustic was determined from the expression

$$I = \frac{E}{S\tau}. \tag{1}$$

The two-photon absorption coefficient β of CaF_2 crystals was also measured using an e-beam-pumped ArF laser [14] emitting 70-ns pulses (Fig. 1b). Experiments with this laser were performed as in Ref. [11] and were similar to those described above.

The method of nonlinear transmission for determining two-photon absorption coefficients of optical materials is based on the measurement of the transmission T of crystals on the laser radiation intensity. The value of β is calculated from the slope of the dependence of the inverse transmission $1/T$ on I. We measured the transmission of crystals by a calorimetric method and calculated T from the expression

$$T = \frac{E_{\text{out}}}{E_{\text{in}}}, \tag{2}$$

where E_{out} and E_{in} are laser energies transmitted through and incident on the crystal, respectively.

The value of T was measured in the following way. First, a series of measurements was performed for 5–10 laser pulses in the absence of a sample and the average ratio $q_0 = \langle (E_2/E_1)_0 \rangle$ of the readings of the first (E_1) and second (E_2) calorimeters was calculated. Then, a sample was place at the focus of the lens and we calculated the ratio $q_{\text{m}} = \langle (E_2'/E_1)_{\text{m}} \rangle$ after a new series of laser pulses. The sample was not displaced during the measurements if no breakdown was observed. The ratio q_{m}/q_0 gives the transmission T for the given average value E_2 or for the value of I calculated from (1).

The value of E_2 was varied by placing filters – plane semi-transparent dielectric mirrors in front of the lens. The transmission T of the sample was measured for each filter. The values of T for $I \sim 1$ MW cm^{-2} were measured by placing samples not at the lens focus but directly behind the lens, where the cross-sectional area of the laser beam was ~ 2 cm^2. The values of $T(0)$ were measured with a spectrophotometer. These data gave the the dependence $T(I)$.

In some experiments, we used a lens with a focal distance of 40 cm instead of 111 cm. In this case, we managed to determine reliably the laser threshold for the sample-surface breakdown. The breakdown threshold was determined as the maximum laser radiation intensity at which no damage of the sample surface was observed.

The value of β was calculated from the experimental dependence $T(I)$ in the following way. If the linear absorption α of a sample is low, i.e., $\alpha l \ll 1$ (l is the sample thickness), the slope of the dependence $\Delta(1/T)/\Delta I$ is related to β by the expression [12]

$$\frac{\Delta(1/T)}{\Delta I} = \beta \frac{l}{(1-R)K}. \tag{3}$$

This gives

$$\beta = \frac{\Delta(1/T)}{\Delta I} \frac{(1-R)}{l} K, \tag{4}$$

where K is the coefficient depending on the laser pulse shape and the distribution of the laser radiation intensity over the caustic cross section; and R is the reflectivity for the sample face at a given wavelength. In the case of a rectangular pulse shape and the uniform distribution of the laser radiation intensity over the caustic radius on the sample surface [dependence $I(r)$], the coefficient $K = 1$. For the Gaussian distributions $I(t)$ and $I(r)$, this coefficient is $2^{3/2}$. We calculated the two-photon absorption coefficient β of CaF_2 from expression (4).

When linear absorption of light in samples cannot be neglected, the expression for β becomes more complicated:

$$\beta = \frac{\Delta(1/T)}{\Delta I} \frac{\alpha e^{-\alpha l}}{(1 - e^{-\alpha l})} (1-R)K. \tag{5}$$

We used this expression for calculating β from the experimental data obtained for BaF_2 and Al_2O_3.

3. Results of measuring β

The two-photon absorption coefficient was measured for high-purity CaF_2, BaF_2, and Al_2O_3 crystals, which were synthesised at the All-Russian Scientific Center, S.I. Vavilov State Optical Institute.

3.1 Results for CaF_2

Fluorite samples were parallelepipeds with faces of size $18 \times 20 \times 22$ mm, whose surfaces were polished up to the III purity class. The quality of crystals was verified for crystal samples cut of the initial CaF_2 crystal by exposing them to an electron beam (an EL-1 setup [14]). After ~ 1500 of the ~ 280-keV electron pulses producing the total energy density of ~ 2400 J cm^{-2} on the sample surface, the residual absorption of the samples did not exceed 1 % at the maximum of the absorption band of F-centres at 390 nm. The transmission of the samples at 193 nm almost did not change after such irradiation. This demonstrates a high quality of fluorite.

The experimental dependence of $1/T$ on I for a sample irradiated by 30-ns pulses from an ArF laser is shown by circles in Fig. 2a. The straight (trend) line is plotted by the method of least squares. From the slope of this curve and expression (4), we obtain $\beta = 2.2$ cm GW^{-1} for $K = 2.8$.

We obtained similar dependences for this fluorite sample irradiated by 70-ns pulses. One of them is shown in Fig. 2b. In this case, the value of β was 2.7 cm GW^{-1} for $K = 2.8$.

The error of measurements of β by this method, which did not exceed 40 %, is mainly determined by the uncertainty in the coefficient K related to the shape of laser pulses (Fig. 1). For a long (close to rectangular) 70-ns pulse, the value of K should decrease because the pulse intensity at its maximum is almost constant for a long time. We calculated

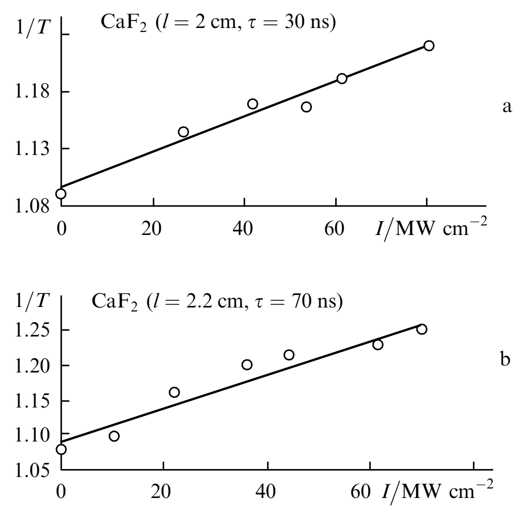

Figure 2. Dependences of the inverse transmission $1/T$ of 2-cm thick CaF_2 samples irradiated by 30-ns (a) and 70-ns (b) pulses from an ArF laser on the laser radiation intensity.

β earlier for such pulses using the value $K = 2$ [7, 11]. For such a coefficient K, the value of β obtained from the experimental data in Fig. 2b is 2 cm GW^{-1}. Thus, we can assume that the values of β for high-purity fluorite irradiated by 30- and 70-ns pulses are virtually the same and equal to 2.2 ± 0.8 cm GW^{-1}.

The breakdown threshold for the 3–4-mm^2 surface of fluorite samples irradiated by 30- and 70-ns pulses was in the region between 90 and 100 MW cm^{-2}. This threshold limited the ranger of laser radiation intensities used in experiments presented in Fig. 2.

The value of β measured earlier for CaF_2 crystals (having an inferior quality than out crystals) irradiated by 193-nm, 60-ns pulses was 3.2 cm GW^{-1} [7]. According to Refs [9, 10], the coefficient β measured by different methods upon irradiation of samples by 1-ns pulses from ArF lasers was 1–4 cm GW^{-1}. The value of β strongly depends on the purity of fluorite crystals [7, 10], increasing with the content of impurities. For fluorite crystals irradiated by picosecond pulses from an ArF laser, $\beta \approx 0.3$ cm GW^{-1} [8].

The analysis of results of different papers made in Ref. [10] showed that the dependence $\beta(\tau)$ is linear for τ changing from $\sim 10^{-12}$ to $\sim 10^{-7}$ s. Our data show that the value of β at 193 nm for nanosecond pulses can change only very weakly, if at all. The reason for a strong increase in the value of β for fluorite on passing from picosecond to nanosecond pulses is analysed in detail in papers [1, 2], and we will not discuss here this question.

3.2 Results for BaF_2

The BaF_2 samples used for measuring β at 193 nm were also of high purity, as testified by their high radiative resistance. After irradiation by the same electron beam as for fluorite, the induced UV absorption in 2-mm thick BaF_2 plates did not exceed 1 %.

The dependence $T(I)$ at a wavelength of 193 nm was measured for 17.5-mm thick BaF_2 plates irradiated by 30-ns pulses. The circles and the averaging straight line in Fig. 3 present the experimental data. The data for $I <$ 100 MW cm^{-2} were obtained using a lens with $f =$ 111 cm. A lens with $f = 40$ cm was used to obtain higher radiation intensities.

The surface breakdown threshold in these experiments was ~ 90 MW cm^{-2}. The data presented in Fig. 3 for laser intensities exceeding 100 MW cm^{-2} were obtained in the case of the surface breakdown. Nevertheless, all the experimental points are well fitted by the averaging straight line. This can be explained by the fact that either absorption of light in the breakdown region is small compared to the total absorption or the surface destruction occurs after the laser pulse. However, additional experiments are required to explain this fact in detail.

By using the experimental value $T(0) = 0.685$ and $R = 0.05$, we obtain from the expression $T(0) = (1-R)^2 e^{-\alpha l}$ the value $\alpha = 0.156$ cm^{-1}. By substituting these values and the slope $[\Delta(1/T)/\Delta I]$ of the curve (Fig. 3) and $K = 2.8$ into (8), we obtain $\beta = 2.3$ cm GW^{-1} for a BaF_2 crystal irradiated by 193-nm, 30-ns pulses. The error in the measuring of β does not exceed 40 %.

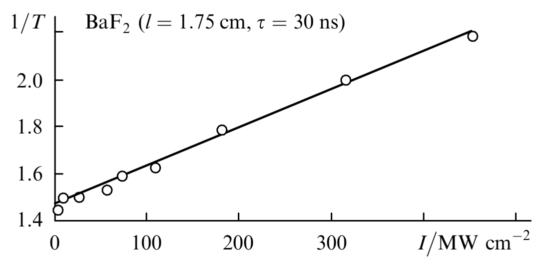

Figure 3. Dependence of the inverse transmission $1/T$ of 1.75-cm thick BaF_2 sample irradiated by 30-ns pulses from an ArF laser on the laser radiation intensity.

The values of β at 193 nm for BaF_2 were measured in Refs [8, 10]. According to Ref. [10], $\beta = 1.2$ cm GW^{-1} for BaF_2 crystals irradiated by 14-ns laser pulses. In this case, the linear absorption of samples was 0.0193 cm^{-1}, which is an order of magnitude lower than in our experiments. In the case of irradiation by short 0.8-ps pulses, $\beta \approx 0.4$ cm GW^{-1} [8]. The results presented above again demonstrate a substantial difference in the values of β obtained upon irradiation of samples by picosecond or nanosecond pulses.

3.3 Results for Al_2O_3

We measured the nonlinear absorption in an 11-mm thick Al_2O_3 crystal disc of diameter 60 mm. This sample had the best UV transmission from the pair of samples for which β was earlier measured at the 248-nm wavelength of a KrF laser [11]. The transmission of this sample at 193 nm is $T(0) = 39$ %.

We measured the dependence T(I) for the Al_2O_3 sample irradiated by 30-ns pulses from an ArF laser. The results and the averaging straight line are presented in Fig. 4. The breakdown of the sample surface was observed at the laser radiation intensity ~ 100 MW cm^{-2}. The transmission of light in the sample drastically decreased after the breakdown. These experimental are not presented in Fig. 4.

The value of β was calculated as for BaF_2 assuming that $R = 0.1$ and the absorption coefficient $\alpha = 0.64$ cm^{-1}. By using the slope of the straight line in Fig. 4 and expression (4) with $K = 2.8$, we obtained $\beta = 5.6$ cm GW^{-1} for the Al_2O_3 crystal irradiated by 193-nm, 30-ns pulses from the ArF laser. The error of measuring β did not exceed 40 %, as before.

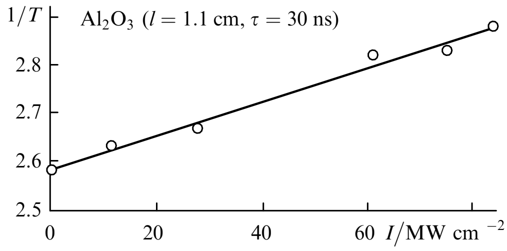

Figure 4. Dependence of the inverse transmission $1/T$ of 1.1-cm thick Al_2O_3 sample irradiated by 30-ns pulses from an ArF laser on the laser radiation intensity.

We are not aware of other data on the nonlinear absorption of leucosapphire samples at 193 nm. To understand the features of the interaction of radiation from an ArF laser with an interesting in many respects optical material such as leucosapphire, it will be quite useful to measure the values of β upon irradiation of leucosapphire by picosecond and nanosecond pulses.

4. Conclusions

We have measured the coefficients of two-photon absorption of radiation from an ArF laser in high-purity CaF_2 crystals irradiated by 30- and 70-ns laser pulses. For BaF_2 and Al_2O_3 crystals, the values of β were measured using 30-ns pulses. The results obtained for CaF_2 and BaF_2 crystals extend the data base for the dependence $\beta(\tau)$ at 193 nm for crystals of different quality. We have found that the values of β are substantially different in the case of irradiation by picosecond or nanosecond pulses. It seems that the results for leucosapphire have been obtain at 193 nm for the first time. We have also determined the surface breakdown thresholds for these samples irradiated by 30- and 70-ns pulses from an ArF laser.

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