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Radiation resistance of optical materials for windows of UV and VUV excimer lasers

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***Abstract*. The behaviour of modern quartz glasses and fluorite is studied experimentally under a prolonged action of the 280-keV electron beam pulses and an overall fluence of up to $\sim$30 kJ cm^{-2}. The induced absorption in all investigated materials saturates with increasing the fluence. The maximum variation of transmission in high-purity CaF_2 samples does not exceed 5 % – 10 % in the wavelength range 120 – 1000 nm. Quasi-stationary absorption in the region of $\sim$180 – 300 nm in the KS-4V quartz glass sample is approximately four times smaller than that in the KU-1 quartz glass and half the value for Corning 7980 glasses.**

Keywords: *optical materials, laser windows, ionising radiation, radiation resistance.*

1. Introduction

Radiation resistance of optical materials (OMs) has become the subject of intense research following the rapid advancement of industrial lasers emitting the UV and VUV spectral ranges. The windows of short-wavelength gas lasers (especially electron-beam-pumped) must have a high radiation resistance because this parameter determines their long service life to a considerable extent. That is why it is so important to study experimentally the radiation resistance of CaF_2 and MgF_2 crystals as well as quartz glasses which are transparent in a broad spectral range. The properties of modern high-purity OM samples of this type sometimes differ quite substantially from the properties of the same materials produced earlier. This necessitates a complex study of such optical materials under the action of ionising and laser radiation.

The aim of this work was to study the properties of Russian quartz glasses KU-1, KS-4V and compare them with Corning glasses and high-purity CaF_2 crystals under the action of an electron beam. The samples were irradiated under conditions closest to the operating conditions of windows in electron-beam-pumped excimer lasers [1 – 5]. We also took into account the fact that the high purity of a number of OMs allows us to use them as prototypes of 'perfectly pure' materials. The results of such investigations may form the basis for refinement of the numerical models of the behaviour of such materials under the action of ionising and laser radiation [6, 7].

For this reason, the energy of electron beams used by us was chosen below the impact defect formation threshold in OMs. In this case, the electron beam produces only electron – hole pairs and other electron excitations, as in the case of two-photon absorption. The electric fields emerging in dielectrics irradiated by charged-particle beams [8] may affect the defect formation. In order to minimise these effects, the OM samples were placed in metal recesses. We also measured the distribution of the absorbed radiation dose from the electron beam used over the thickness of the irradiated samples [1 – 4]; this is necessary for determining the relation between the absorption induced in the OM and the characteristics of ionising radiation. All these fine experimental details have made it possible to obtain the results for the radiation resistance of the above OMs exposed to an electron beam under quite definite irradiation conditions. This is important both from theoretical and experimental points of view.

2. Experimental

Quartz glasses are the main materials for large-size windows of high-power electron-beam-pumped KrF lasers. This determined our interest in studying the properties of these materials. The KU-1 glasses and their foreign analogues (e.g., Corning 7980) belonging to type III glasses are prepared for use in the UV range. The hydroxyl (OH) concentration in these glasses amounts to approximately 1000 ppm, while the concentration of other impurities (mainly chlorine) varies from $\sim$200 ppm (KU-1) to 20 ppm (ArF grade Corning 7980) [3, 4, 9 – 11]. Apart from these glasses, a new high-purity Russian KS-4V quartz glass sample was also tested [9]. This type of glass was obtained at the I.V. Grebenshchikov Institute of Silicate Chemistry, RAS. Commercial production of this glass has begun at the Miass machine-building plant. This is a type IV glass [9, 10]. The impurity concentration (of 15 main elements) in this glass is less than 0.5 ppm. The hydroxyl concentration is less than 0.1 ppm, while chlorine atom concentration is less than 20 ppm [9]. Comparative radiation characteristics of all these glasses under identical conditions of irradiation may be found useful in many respects.

High-purity fluorite crystals studied by us and suitable for operation with UV and VUV laser radiation were prepared at the S.I. Vavilov State Optical Institute. The impurity concentration in these crystals was 15 – 17 ppm [1, 2, 5]. (Other information concerning the samples will be given in the description of results.)

Glass samples had a diameter of 12 mm and a thickness of 3 – 4 mm. The plate surfaces were polished, as a rule,

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according to III surface finish class. Optical materials were tested under the action of an electron beam on the electron-beam-pumped ELA laser setup [12]. In these experiments the laser chamber was removed from the device and a special assembly with samples under investigation was placed at the electron gun foil [1 – 5]. The assembly consisted of a thick duralumin plate with recesses milled for each sample. Samples were covered from the side of incidence of the electron beam by a single layer of 14-μm-thick Ti foil. Behind the foil, the samples were irradiated in the so-called first regime when the electron energy was ~280 keV, and the energy density per pulse was $F_1 \sim 2$ J cm^{-2}. Some of the samples were covered by an additional Ti foil filter of thickness 50 – 100 μm. The electron beam energy at the surface of these samples, which were irradiated in the so-called second regime, did not exceed 100 keV while the value of F_1 was varied in the range 0.2 – 0.8 J cm^{-2}.

The electron gun of the ELA setup worked in the pulsed regime at a frequency $\sim 5 \times 10^{-3}$ Hz. In the course of a working day, between 50 and 150 shots were fired from the gun. The electron energy behind the foil of the electron gun was about 280 keV, the beam current density was up to 200 A cm^{-2}, and the pulse duration was 80 ns. The total electron beam energy behind the output foil was 250 – 300 J for a cross-sectional area of 4 × 22 cm, while the energy density F_1 at the foil attained values of up to 3 J cm^{-2}. The assembly with samples was placed at a distance of 25 mm from the dividing foil to reduce small-scale inhomogeneities in the electron beam energy density. In this region, the value of F_1 was about 2.5 J cm^{-2}, while the cross-section area of the electron beam with such fluence was higher than 70 cm^2. This made it possible to irradiate up to 25 samples simultaneously.

The transmission of samples in the range 200 – 1000 nm was measured before irradiation and after a series of pulses with the required total fluence F with a Genesis-2 spectrophotometer (Spectronics). In the spectral range 120 – 240 nm, the transmission was measured with a VMR-2 monochromator. The transmission spectra were recorded in the form of digital tables with a wavelength step of 3 nm. This made it possible to carry out computer processing of the results, which simplified their analysis.

The first step in this analysis was the construction of the optical density (OD) spectra of the samples from their transmission spectra. The value of OD at a particular wavelength λ was calculated from the expression

$$\mathrm{OD} = \ln(T_0/T), \quad (1)$$

where T_0 and T are the sample transmission before and after irradiation by an electron beam or some other action.

3. Electron-beam-induced long-lived absorption in quartz glasses

Figure 1 shows the typical transmission spectra of some of the tested samples before and after electron-beam irradiation in the first regime and the corresponding electron-beam induced optical density spectra OD (λ) of the samples. Note that VUV transmission cutoffs practically coincide for type III glasses (KU-1 and Corning samples) before irradiation. This cutoff is determined by the concentration of the hydroxyl group (about 1000 ppm for all these glasses). The OH concentration in KS-4V glass is almost four orders of magnitude lower and its VUV transmission

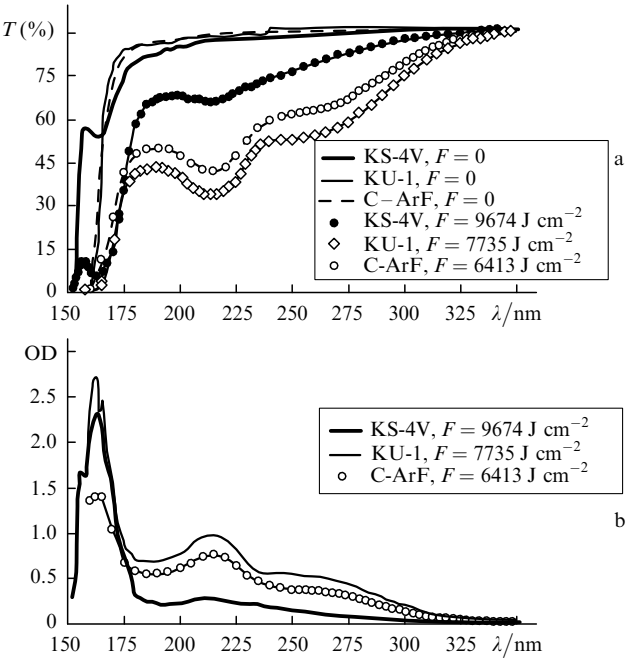

Figure 1. (a) Transmission spectra of the KS-4V, KU-1 and Corning 7980 (ArF grade – C-ArF) glass samples before and after exposure to the electron beam from the ELA setup and (b) induced optical density spectra for the same samples for various values of the beam fluence F.

cutoff is displaced towards the shortwave region by approximately 10 nm.

One can see from Fig. 1 that typical variations in the transmission spectra of the samples after irradiation by the electron beam are observed in the region with $\lambda < 350$ nm (in the visible range, the transmission remained unchanged right up to ~1000 nm). The transparency loss is quite large for all glasses exposed to the electron beam in the shortwave region. This must be taken into account while developing industrial electron-beam excimer lasers.

The electron-beam-induced OD spectra presented in Fig. 1b are almost identical to the spectra formed under the action of other ionising radiation [13 – 15]. Note that the ratio of the intensities of the main absorption lines in the range 180 – 350 nm is preserved for each grade of glass over a wide range of fluences. This fact facilitates the description of the dependences of the induced absorption spectra in this region on the ionising radiation parameters (in particular, on the electron beam fluence); it is sufficient to find this dependence for one of the wavelengths. In our case, it is convenient to do so at $\lambda = 250$ nm.

Figure 2 shows the dependences of OD for $\lambda = 250$ nm (OD_{250}) on the fluence for glass samples Corning 7980 (Standard grade – C-0, KrF-grade – C-KrF, ArF-grade – C-ArF), KU-1 and KS-4V. These dependences were obtained under identical irradiation conditions on the ELA setup in the first regime with fluences up to 6.5 kJ cm^{-2}. The results of measurements for KU-1 and KS-4V glasses obtained in earlier experiments [3, 4] under analogous conditions are also shown for comparison.

One can see from Fig. 2 that an increase in the electron beam fluence leads to saturation of induced absorption for all tested glasses. In the saturation mode, the KS-4V glass displayed minimum absorption. The highest value of the optical density $\mathrm{OD}_{250}^{\max}$ attained in these experiments for this glass was 0.15. Among type III glasses, Corning 7980 (ArF-

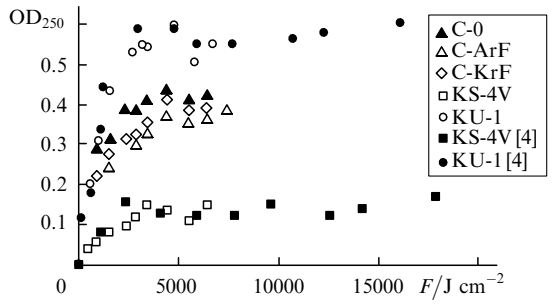

Figure 2. Dependence of the induced optical density at $\lambda = 250$ nm on the electron beam fluence for various glass samples; ■ and ● are the results of analogous measurements borrowed from [4].

grade – C-ArF) has the highest radiation resistance. For this glass $OD_{250}^{max} = 0.37$. For the remaining glasses, an increase in OD_{250}^{max} was observed upon an increase in the chlorine impurity concentration. The value of OD_{250}^{max} was 0.6 for the KU-1 glass with the highest contamination in this impurity.

It was found earlier that induced absorption in KU-1 glass on the quasi-stationary region in the UV range is proportional to the mean radiation power of the electron beam [3, 4]. An analogous dependence is also observed for other glasses of this type.

The dependence of OD on the mean electron beam radiation power in the quasi-stationary region for KS-4V glass is much weaker. For a nearly tenfold difference in radiation powers, the saturation absorptions in this glass differ approximately by a factor of 1.5 [4].

The dependences of the induced optical density on fluence show that the production of long-lived colour centres under the action of an electron beam is a nonlinear process that cannot be described by a single parameter – the efficiency of production of the centres. The production of centres is accompanied by their relaxation. Figure 3 shows the time dependence of absorption in Corning 7980 samples after the last electron beam pulse. Similar time dependences of OD were also observed for KU-1 and KS-4V glasses. The extrapolated dependences of OD on time t at 250 nm (straight lines in Fig. 3) are described by the expressions

$$OD_{250} = A - B \ln t, \qquad (2)$$

where t is measured in seconds and the values of corresponding coefficients A and B are shown in Table 1 for all investigated glasses.

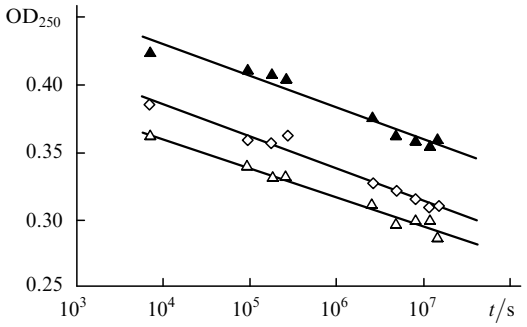

Figure 3. Decrease in OD_{250} with time after exposure of Corning 7980 samples to electron beam radiation. Notation for samples is the same as in Fig. 2.

Table 1.

Type of glass	A	B
KU-1	0.82	0.024
C-0	0.53	0.01
C-KrF	0.45	0.009
C-ArF	0.45	0.0093
KS-4V	0.18	0.0045

These coefficients were obtained from the experimental results on the time interval $\sim 4 \times 10^3 - 10^7$ s on samples held in dark at room temperature. It should be emphasized that the results on OD relaxation were obtained on samples with a very strong nonuniformity in the distribution of their absorbed dose of the electron beam radiation over thickness [1 – 5]. The storage conditions for irradiated samples are also important. For example, heating of Corning and KU-1 glass samples for about 20 hours at a temperature of about 400 °C almost completely eliminates the induced absorption. A much longer time is required for relaxation of absorption in the KS-4V glass. Optical irradiation also affects the induced absorption relaxation.

The obtained results show that the KS-4V glass is the most suitable among all tested materials for preparing windows of electron-beam-pumped excimer UV lasers in view of its high radiation resistance.

4. Electron-beam-induced absorption in fluorite

The first results of our investigations of the behaviour of high-purity CaF_2 and MgF_2 samples under the action of electron beam from the ELA setup are presented in [1, 2, 5]. These experiments were continued and some new results were obtained for CaF_2.

Figure 4a shows a typical consolidated picture of transmission spectra for one of the six high-purity CaF_2 samples irradiated between March 2003 and July 2005, as well as the values of $F > 26$ kJ cm^{-2} accumulated by the end of this cycle. Note that all the samples in this group are 10×10 mm in size, which differs from the size of the spectrophotometer window (5×11 mm). For this reason, the inevitable and significant displacements of the samples during their fixation to the spectrophotometer window led to a parallel displacement of the spectrum towards lower values of T, which can be seen clearly in Fig. 4a. The value of such a displacement varies within 5 %. This is a systematic error which is comparable to the induced absorption.

In this connection, a new sample prepared from the central part of the boule of diameter 100 mm was added to the old group of CaF_2 samples at the last stage of our experiments. According to the data furnished by the manufactures (Vavilov State Optical Institute), this material had an extremely high purity. The results on the new CaF_2 sample of size $20 \times 20 \times 5$ mm (working No. 2/3) are shown in Fig. 4b. Note that like all the samples of CaF_2, this sample was always irradiated in the extremely hard first regime (with a single 14-μm-thick Ti foil as a filter) with a fluence per pulse in the interval 2 – 2.4 J cm^{-2} and an electron energy of about 280 keV. Figure 4 also shows a parallel shift of the spectra. However, this shift does not exceed 0.5 %, which is close to the calibration error for the spectrophotometer. At this level, the dustiness of the samples may be noticeable.

Figure 5 shows the optical density spectra for sample No. 2/3 after various time intervals following irradiation by

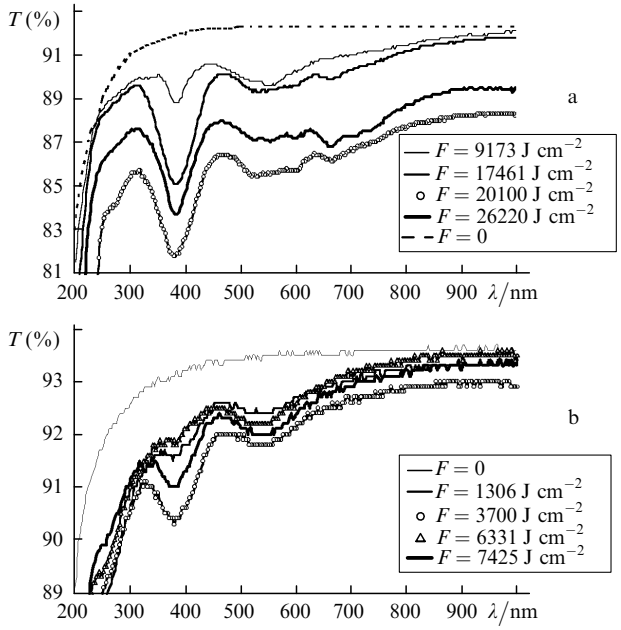

Figure 4. Transmission spectra of one of the six 'old' CaF_2 samples (No. 8) (a) and sample No. 2/3 (b) after exposure to electron beams with different fluences.

an electron beam with $F = 7425$ J cm^{-2}. These spectra are slightly different from the analogous spectra for the old group of samples [5] in that they contain a new absorption band with a peak at $\lambda = 260$ nm and have a more clearly manifested band with a peak near 540 nm. These bands remained practically unchanged during storage of the sample for one year.

The absorption band with the highest intensity and with a peak at $\lambda = 379$ nm belongs to the F-centres [16]. It is seen clearly for all CaF_2 samples (see Fig. 4) and was therefore used to characterise their radiation resistance. The dip in the transmission spectra at $\lambda = 379$ nm was chosen for a quantitative description of specific curves. This dip was defined as

$$\Delta D = [(T_1 - T_m) + (T_2 - T_m)]/2. \quad (3)$$

where T_m is the transmission at $\lambda = 379$ nm, and T_1 and T_2 are the maximum values of the sample transmission at the left and right of the dip. In view of the small value of ΔD, the relation $\Delta D = \Delta\mathrm{OD}$ was observed. Using this parameter for a quantitative description of the radiation resistance of fluorite samples, we can eliminate the systematic error associated with the parallel shift of the spectra for various transmission measurements.

No explicit dependence of the induced absorption on F was observed for all the CaF_2 samples studied by us. This could be due to a rapid relaxation of the induced colour centres after irradiation and the difference in delays in measurement of transmission of samples after irradiation, which varied from 2 h to 5 days in various experiments. Figure 5 clearly shows the relaxation of the absorption band with a peak at $\lambda = 379$ nm for sample No. 2/3. To find the effect of the delay between termination of irradiation and measurement of transmission, all fluorite samples were registered two hours after the last shot, then after 1, 2 and 3 days, after one month and after one year. These results were used for plotting the time dependences of ΔD for sample No. 2 and ΔD averaged over the six old samples (Fig. 6). One can see that ΔD for the samples decreases on the average by 30 % during the first day after irradiation, and by half after 3 days. The value of ΔD for old samples decreased on the average by a factor of 3.2 during one year.

As in the case of quartz samples, the extrapolated time dependences of ΔD at 379 nm (straight lines in Fig. 6) are described by formula (2). The averaged values of the coefficients A and B for 'old' samples are 0.0533 and 0.0025, while the corresponding values for sample No. 2/3 are 0.0238 and 0.0014.

The decrease in the value of absorption in the F-band with time must be accompanied by a decrease in concentration, and hence a decrease in absorption of H centres whose bands are located in the range of 310 and 700 nm (see [16], p. 115).However, this absorption is small and cannot be seen. The observed bands with peaks at $\lambda = 260$ and 540 nm do not belong to Frenkel defects. They may be associated with oxygen impurity diffusing into the samples during irradiation [5, 17] or may belong to other impurity or surface colour centres [18, 19]. Our comparison of the irradiated and unexposed surfaces of CaF_2 under an electron microscope revealed a considerable increase in the roughness of the exposed surface. Similar effects were observed earlier during exposure of CaF_2 samples to synchrotron radiation [18, 19]. We did not observe any change in the structure of electron-beam-irradiated surfaces of quartz samples as wells as MgF_2 and Al_2O_3 samples.

The parameter ΔD was also used for analysing the growth of electron-beam-induced absorption in CaF_2 upon an increase in F. Figure 7 shows the entire body of data on ΔD averaged over the group of six 'old' samples, as well as data for sample No. 2/3 for various values of F. All the results shown in Fig. 7 were obtained after a delay of one

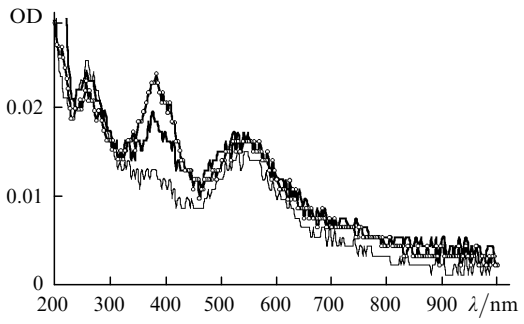

Figure 5. OD spectra of CaF_2 sample No. 2/3 after two hours (○), one day (bold curve) and one month (fine curve) following irradiation by an electron beam with $F = 7425$ J cm^{-2}.

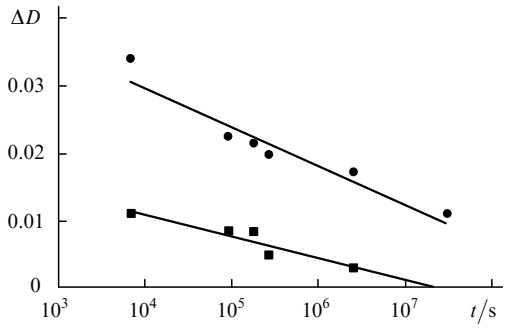

Figure 6. Relaxation of ΔD at $\lambda = 379$ nm for sample No. 2/3 (■) and of ΔD averaged over six 'old' CaF_2 samples (●).

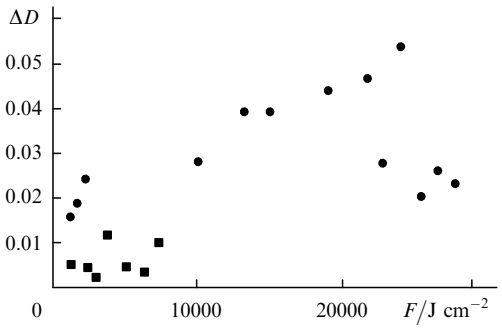

Figure 7. Dependence of ΔD at $\lambda = 379$ nm on fluence for sample No. 2/3 (■), as well as ΔD averaged over six 'old' CaF_2 samples (●).

day in the measurements of transmission of the samples after the termination of a series of electron beam pulses. But even in this case, a nearly two-fold spread is observed in the results for close values of F. An analysis of the reasons behind such a spread showed that the results for old samples with $\Delta D \sim 0.025$ were obtained in series of irradiation with an average shooting rate at a level of 50 – 70 pulses per day. Higher values of ΔD were observed for shooting rates ~100 – 150 pulses per day. An analogous correlation between ΔD and the series-averaged radiation power was also observed for sample No. 2/3, but for lower peak values of ΔD.

The obtained results for high-purity CaF_2 samples lead to the following conclusions.

(i) The electron-beam-induced absorption at intrinsic defects in fluorites attains saturation whose level is determined by the average radiation power. This is due to a rapid relaxation of the pairs of F and H defects formed in the process.

(ii) In extremely high-purity CaF_2 samples, the highest values of the registered absorption after electron beam irradiation on the ELA setup did not exceed 5 % – 10 % in the range 120 – 1000 nm.

(iii) The main part of the electron-beam-induced long-lived absorption in CaF_2 is associated with the impurities existing in the crystal or diffusing into the bulk from the surface during irradiation.

(iv) The high-purity CaF_2 windows ensure a long service life even for electron-beam excimer lasers operating in the UV and VUV regions.

5. Conclusions

We have studied experimentally the behaviour of modern quartz glasses and fluorites intended for windows of UV and VUV gas lasers and subjected to prolonged action of an electron beam with an electron energy of less than 280 keV and a fluence $F \leqslant 30$ kJ cm^{-2}. The limiting variations in the transmission of high-purity samples of CaF_2 exposed to an electron beam with $F \leqslant 30$ kJ cm^{-2} did not exceed 5 % – 10 % in the visible, UV and VUV ranges. Windows made of such CaF_2 crystals may ensure reliable and long-term operation of both electric-discharge and electron-beam-pumped excimer lasers with a radiation wavelength exceeding 150 nm.

Experiments have shown that the electron-beam-induced absorption in the range ~180 – 300 nm in the new Russian quartz glass of type KS-4V was found to be about one-fourth of the absorption observed in KU-1 glass and less than half of the absorption for Corning 7980 glasses. This makes the KS-4V glass a promising material for manufacturing windows of high-power UV lasers.

In experiments on radiation resistance of optical materials, we used an electron beam with electron energies below the destruction threshold of material as a result of direct knocking out of lattice atoms. For the electron beam used in the study, we measured the distribution of the absorbed dose over the thickness of the absorber. These features of the experiments make it possible to use the results for refining the numerical models describing the long-term behaviour of OMs under the action of ionising and high-intensity laser radiation in the UV and VUV regions, which is a powerful source of ionisation of materials in two-photon processes.

The experimental data on the radiation resistance of modern quartz glasses and fluorite presented in this work are required for a deeper understanding of the physics of radiation processes and for their simulation. These results will also be useful for manufacturers of optical materials and designers of lasers and other sources of UV and VUV radiation.

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References

1. Mironov I.A. et al. *Proc. SPIE Int. Soc. Opt. Eng.*, **5479**, 135 (2004).
2. Sergeev P.B. et al. *Proc. 12th Int. Conf. Radiation Phys. and Chem. of Inorganic Mater.* (Tomsk, 2003, p. 82).
3. Sergeev P.B. et al. *Proc. SPIE Int. Soc. Opt. Eng.*, **5506**, 81 (2004).
4. Sergeev P.B. et al. *J. Opt. Technol.*, **71**, 93 (2004).
5. Sergeev P.B. et al. *J. Opt. Technol.*, **72**, 85 (2005).
6. Kurbasov V.S., Sergeev P.B. *Kvantovaya Elektron.*, **30**, 703 (2000) [*Quantum Electron.*, **30**, 703 (2000)].
7. Sergeev P.B. *Kvantovaya Elektron.*, **32**, 344 (2002) [*Quantum Electron.*, **32**, 344 (2002)].
8. Boev S.G., Ushakov V.Ya. *Radiatsionnoe nakoplenie zaryada v tverdykh dielektrikakh i metody ego diagnostiki* (Radiation-induced Charge Accumulation in Solid Dielectrics and Methods of its Diagnostics) (Moscow: Energoatomizdat, 1991) p. 12.
9. Cheremisin I.I., in *Fizikokhimiya silikatov i oksidov (sbornik RAN)* (Physics and Chemistry of Silicates and Oxides) (Collected works by the Russian Academy of Sciences) (St. Petersburg: Nauka, 1998) p. 253.
10. Leko V.K., Mazurin O.V. *Svoistva kvartsevogo stekla* (Properties of Quartz Glass) (Leningrad: Nauka, 1985).
11. http://www.corning.com/
12. Sergeev P.B. *J. Sov. Laser Research*, **14** (4), 237 (1993).
13. Jani M.G., Hallibuto L.E. *J. Appl. Phys.*, **56**, 942 (1984).
14. Marshall C.D., Speth J.A., Payne S.A. *J. Non-Cryst. Sol.*, **212**, 59 (1997).
15. Latkowski J.F. et al. *Fusion Sci. Technol.*, **43**, 540 (2003).
16. Stoneham A.M. *Theory of Defects in Solids: the Electronic Structure of Defects in Insulators and Semiconductors* (Oxford: Clarendon Press, 1975; Moscow: Mir, 1978).
17. Cheredov V.N. *Defekty v sinteticheskikh kristallakh fluorita* (Defects in Synthetic Fluorite Crystals) (St. Petersburg: Nauka, 1993).
18. Gatto A. et al. *Proc. SPIE Int. Soc. Opt. Eng.*, **4932**, 366 (2002).
19. Guenster S. et al. *Proc. SPIE Int. Soc. Opt. Eng.*, **4932**, 422 (2002).