Change of absorption spectra structure in MgF_2 under e-beam and UV light Irradiation[1]

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Abstract – In the paper transmission and absorption spectra of MgF_2 samples irradiated by the e-beam and laser radiation at 248 and 372 nm are analyzed. From this spectra 13 individual bands of absorption have been identified with the help of Alencev- Fok's method. The peak position and width of this band at half-maximum are given. All this bands have been assigned to particular defects of the crystal. The KrF-laser radiation bleaching of residual absorption in MgF_2 samples results in a strong drop of the absorption in the range of 115–280 nm and not large growth of absorption at 300, 400 and 460 nm bands.

1. Introduction

The crystals of MgF_2 have large width of the forbidden zone, 11.6 eV, and high mechanical durability. It makes by their irreplaceable at work with radiation, in particular laser, in the field of wave-lengths < 150 nm. However under action of short-wave radiation the windows from MgF_2 lose the transparency [1–4]. This occurs and at influence of ionizing radiations (IR) [5–10]. So in [5, 6, 8, 10] was shown, that at an irradiation of MgF_2 samples by x-ray and e-beam monotonous increase of absorption occur in them on the whole series of bands. The additional light irradiation of these samples results in essential transformation of the primary absorption bands and occurrence of new. In spite of the long history of study of defects formation in MgF_2 while there is no complete clearness in an belonging of same absorption bands to the own defects of this crystal. And it strongly constrains understanding of physics of defect formation in MgF_2 under ionizing and laser radiation action.

A series of new experimental results on colouring of MgF_2 samples under action of the e-beam, and also on phototransformation of the induced absorption spectra under action of laser radiation at 248 and 373 nm are presented in the given work. The table with the characteristics of the individual absorption bands in MgF_2 is made on the basis of the received results and literary data.

2. Technique of experiments

Several last years we carried out tests for radiation durability of various optical materials for the windows of excimer lasers under influence of an e-beam (EB). The MgF_2 samples were also tested. The results were published [10–12]. For this reason we shall not stop here in details on a technique of these tests. Let's note only the most essential on the tested MgF_2 samples.

The samples by thickness of 3–5 mm and the diameter approximately 12 mm were obtained from S.I.Vavilov's State Optical institute (SOI), Korth Kristalle and Corning. The manufacturer firm of the sample will be marked by the first letter of its name during the further representation of the results. On the data from the manufacturers the samples from Korth Kristalle and Corning have the impurities at the level 20 ppm. At SOI's samples the amount of impurities was approximately on the order more.

The samples were irradiated by e-beam on the setup ELA [13] at 300^0 K. Thus they were placed in niches of a metal plate and are covered with a Ti foil by thickness from 14 up to 80 μm. The thickness of the filter from a foil defines the electron energy and e-beam energy density for a pulse (F_1) reaching up to the samples. The characteristics of the used EB were the following: the electron energy is up to 280 keV, F_1 is up to 2.4 J/cm^2, the pulse duration of 80 ns, the pulse repetition rate is about 20 pulses per house. The common fluency of the irradiation of the samples (F) was defined as the sum of the fluency for each pulse.

Optical absorption measurements were made with a Spectronic Genesis 2 with resolution of 3 nm in the range 200–1000 nm and with VMR-2 in the range 110–240 nm after an irradiation of the samples be EB with required F. Some such transmission spectra of irradiated with various fluency MgF_2 samples are shown in Fig.1. These spectra were registered as the numerical tables $T_i(\lambda_i)$ and were kept in the computer. The plenty of files with such spectra and also MgF_2 samples with e-beam induced absorption of various intensity has collected for all time of tests.

After ending of an irradiation the MgF_2 samples were kept in darkness at room temperature. Periodically they were measured for observation of the absorption relaxation. The experiments on study of influence of the light irradiation on the residual absorption were carried out with a part of these samples. So the additional set of spectra has appeared.

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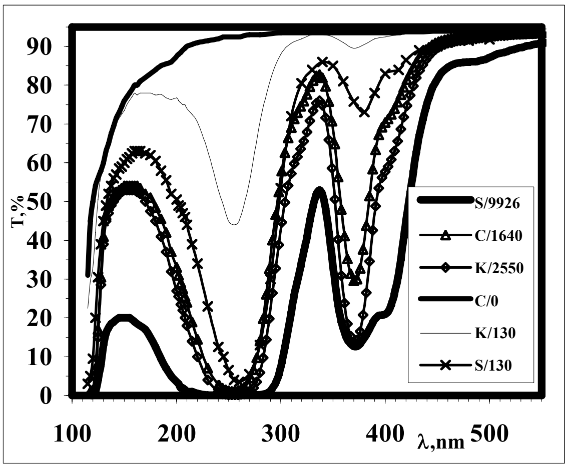

Fig. 1. The typical transmission spectra of the MgF_2 samples after e-beam irradiation with appropriate F (the numbers after / in [J/cm^2])

From transmission spectra the spectra of optical density turned out by point transformation under the formula $OD(\lambda_i)=\ln[T_{0i}(\lambda_i)/T_i(\lambda_i)]$ (T_0 is initial transmission of the sample), Fig. 2. The analysis of all set of these spectra on various MgF_2 samples and will be submitted here.

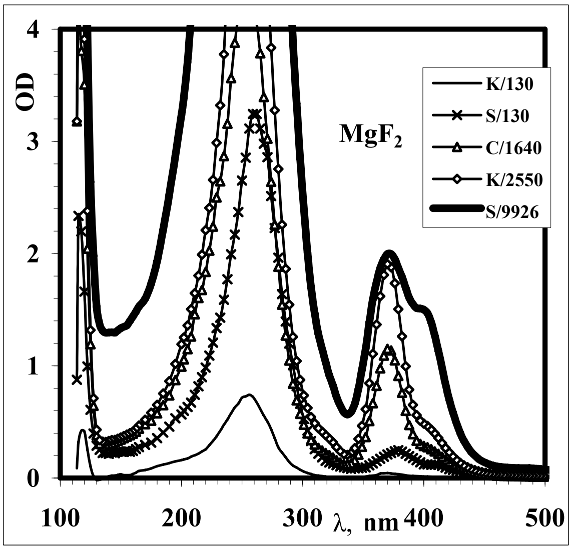

Fig. 2. The OD spectra for the same MgF_2 samples, presented in Fig.1

3. The division of the e-beam induced absorption spectra in MgF_2 on elementary components

The presence of the large set of the induced absorption spectra of MgF_2 with various intensity has allowed to apply Alentcev-Fok's method [14] for allocation of individual absorption bands. Thus the results of works [1–12] were also used. The repeated checks have shown, that practically all allocated bands can be described with the help of a Gaussian shape, that we and have made. The characteristics of all allocated with us bands in this approximation are resulted in the Table 1. The peak position of bands (λ_{max}) here is given in [nm] and [eV]. The full width at half-maximum of the bands ($\Delta\lambda$) in [nm] is shown in the third column. With the help of selection of peak coefficients for these individual bands and their subsequent summation we managed to reproduce the forms practically of all experimental OD(λ) spectra.

Table 1

№	λ_{max} [nm] / [eV]	Δλ [nm]
1	120 / 10.4	13
2	140 / 8.9	40
3	175 / 7.1	26
4	205 / 6.1	30
5	214 / 5.75	35
6	220 / 5.67	50
7	253 / 4.93	43
8	259 / 4.82	32
9	300 / 4.16	22
10	320 / 3.9	30
11	370 / 3.4	28
12	400 / 3.1	48
13	460 / 2.7	60

The allocation of separate spectral lines at once brings an attention to the question on their belonging. Our answer to it is those.

The first absorption line at 120 nm undoubtedly belongs to α-centers. It is on UV transmission edge of the crystal. Intensity of this band monotonously increases with growth of e-beam fluency.

The line with a maximum of 140 nm belongs to the I-centers. Its intensity was insignificant even at greater irradiation, that testifies to low production efficiency of I-centers. Most precisely this line has appeared at KrF-laser bleaching of F-centers.

The lines with maxima at 253 and 259 nm belong to the F-centers with different orientation of its dipole moment in relation to the optical axis [3,5–9]. In real spectra this lines form the strongest absorption band with maximum on wavelengths in range 253–265 nm [1–12]. In our experiments the value of OD(256 nm) is increased practically linearly with growth of F [10]. The slope of these lines was the less at the purest samples. Linear dependence of absorption on the F-centers with growth of the absorbed doze from x-ray and e-beam was observed and earlier [5–6, 8].

The lines at 220, 214 and 205 nm are, apparently, K-and L- absorption bands of the F-centers.

The strong absorption band with a maximum at 370 nm belongs to the M-centers (pair of F-centers) [1–8]. In our experiments with growth of e-beam fluency the value of OD(370 nm) in samples grew proportionally to $[OD(256nm)]^2$. The same it was observed earlier [6]. Such dependence is characteristic feature of the M-centers [15].

The bands at 300, 320 and 400 nm are assigned to the M-centers or their charging components [1–8].

The new band with a maximum at 460 nm, in our opinion, belongs to the F_3-centers.

3. Phototransformations of absorption spectrum of MgF_2

The mercury lamp RGD-2, KrF-laser and frequency doubled Ti:sapphire laser are used as a light source in the experiments on studying of behavior of colors absorption in MgF_2 under action of light

In experiments with a mercury lamp the SOI's samples irradiated by EB with F=1240 J/cm^2 were placed on a distance of 6 cm from a tube. Time of unitary illumination does not exceed 30 minutes. Registration of a spectrum was led in range 200–1000 nm. Characteristic changes of OD spectra are shown in Fig. 3.

After the first experiment with 3-minute illuminating there was a small reduction of absorption on long-wave edge of the basic absorption band of the F-centers. Thus absorption at 370 and 400 nm bands, which intensities have practically coincided, has sharply increased. After following 30-minute illuminating the long-wave part of a F-band reduced even more, the band at 370 nm has a little bit rise and, surprisingly, is a little more, intensity of 400 nm band has decreased. At following cycles of illuminating the structure of last spectrum practically did not vary. It has found a new stationary condition.

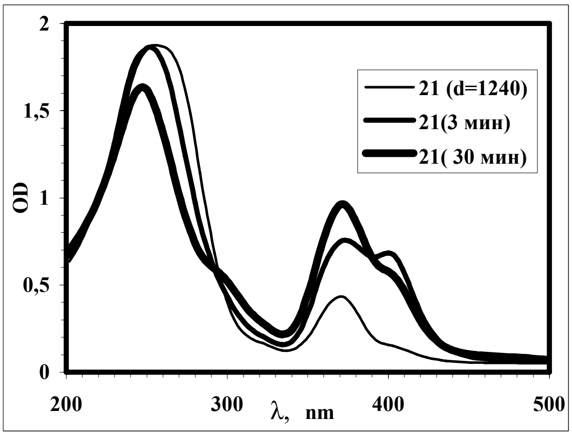

Fig. 3. E-beam induced OD spectra in sample SOI №21 after F=1240 J/cm^2 (a thin line), after illuminating by a Hg-lamp during 3 minutes (an average line), and 30 minutes (a thick line)

The KrF-laser radiation (248 nm) of setup ELA [13] were used in the experiments on selective bleaching of the F-band. The energy density of a laser radiation (LR) on the samples for a pulse was 0.1 J/cm^2 at pulse duration of 80 ns. The total LR fluency for the first and second series of laser pulses were 5 and 6 J/cm^2 accordingly. In Fig. 4 OD spectra of one of the Corning's samples irradiated by e-beam with F=3080 J/cm^2 and was in darkness before laser irradiation about one year (curve C2) are presented. Curve (C2+5J/cm^2) and curve (C2+11J/cm^2) is spectra of the same sample after the first and second series of bleaching laser pulses. A difference between the first and the second, and the second and third spectra are designated, accordingly, DOD1 and DOD2.

It is visible, that after the first series of pulses the absorption very strongly falls at all lines in range <280 nm. Approximately equally falls the absorption of F-centers and α-centers (120 nm). It was also observed an insignificant falling of absorption at 370 nm band. Growth of OD was observed at 300, 400 and 460 nm. After the second illuminating a direction of changes in spectral bands are kept (see DOD2), but intensity of all processes is sharply reduced. Exception is the 300 nm band the growth of which is kept.

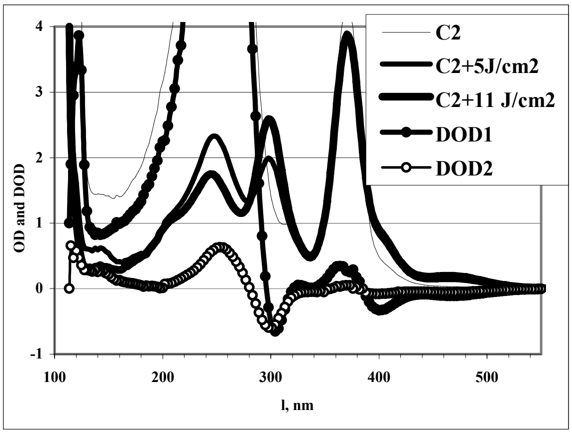

Fig. 4. The absorption spectrum of Corning's sample #2 with F=3080 J/cm2 (a thin line) and after its irradiation by KrF-laser with total fluency 5 J/cm^2 (an average line) and 11 J/cm2 (a thick line). Lines with black marks is a difference between the first and the second spectra, white marks is a difference between the second and the third one

The OD spectrum (C2+5 J/cm^2) is very similar to a curve received in work [7] after illuminating by low-power light with λ=254 nm. But in our case we have not observed the growth, we saw the falling of absorption at 370 nm. It specifies that concentration of M-centers causing the absorption at 370 nm can become saturated.

Selective influence to the 370 nm band was led by frequency doubled Ti : sapphire laser (λ=372 nm). The Korth's sample with F=2680 J/cm^2 was irradiated by this LR. The LR energy density for a 50 fs pulse was 2 mJ/cm^2, pulse repetition rate was 10 Hz. The total LR energy density for a series of pulses was 10 J/cm^2. The occurred changes in the T spectrum of sample are presented in Fig. 4. It is visible, that all changes in transmission occur basically in range 300–470 nm. The T at the 320 and 370 nm bands sharply increases, and at 400 nm sharply falls. From here follows, that selective illumination in 370 nm band leads to its partial bleaching, but the absorption at 400 nm band increases. In 5 days after that experiment the transmission at 400 nm has increased from 53 up to 57 %, and T at 370 nm has fallen from 62 up to 49 %.

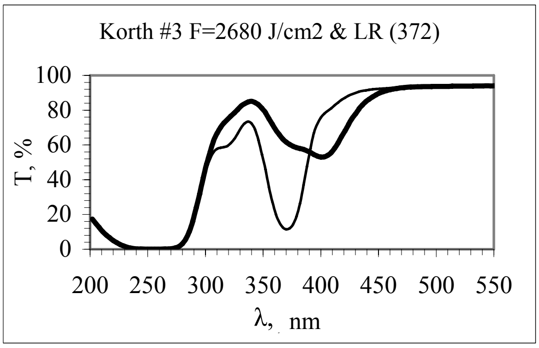

Fig. 4. The transmission spectrum of Korth #3 specimen after e-beam irradiation with F=2680 J/cm^2 (a thin line) and after its laser irradiation (λ=372 nm) with total energy density 10 J/cm^2

5. Conclusion

On the basis of own results and literary data systematization of absorption lines of color centers in MgF_2 in range 110–1000 nm is executed. At the same time the new lines at 120, 140, 205, 214, 220 and 460 nm are revealed.

It was shown experimentally, that the selective illumination by the KrF-laser radiation in a F-band of strongly colored by e-beam MgF_2 sample leads to a significant bleaching not only this, but also other bands in range 115–280 nm. Thus the absorption and at 370 nm was decreased, accompanied by small increasing in the absorption at 300, 400 and 460 nm.

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References

[1] L.P. Shishatskaya et.al. OMP. **69** (1972).
[2] A. Apinov et.al. OMP. **10** (1983).
[3] E.V. Zhukova et. al. Optics and Spectroscopy. **81**, 236 (1996).
[4] G.N. Gerasimov et.al. J. Opt. Technol. **69**, 158 (2002).
[5] R.F. Blunt, M.I.Cohen, Phys. Rev. **153**, 1031 (1967).
[6] W.A. Sibley, O.E.Facey, Phys. Rev. **174**, 1076 (1968).
[7] O.E. Facey, W.A.Sibley, Phys. Rev. **186**, 926 (1969).
[8] M.V. Nikanovich et. al. Optics and Spectroscopy. **60**, 236 (1996).
[9] L.A. Lisitsyna et. al. Optics and Spectroscopy. **96**, 230 (2004).
[10] P.B. Sergeev et.al. J.Opt.Technol. **72**, 493 (2005).
[11] P.B. Sergeev, I.A.Mironov et.al. *in Proc.of 12th Intern. Confer. on Rad. Physics and Chemistry of Inorganic Materials.* 2003, p.82.
[12] I.A. Mironov, V.M.Reiterov et.al. Proc. of SPIE, **5479**, 135 (2003).
[13] P.B. Sergeev. J. of Soviet Laser Research. **14**, 237 (1993).
[14] M.V. Fok. Proc. of P.N.Lebedev Physical Institute. **59**, 3 (1972).
[15] A.A. Predvoditelev et.al. *Physics of crystals with defects.* Moscow, MGU, 1986, p.37.