Photochemical changes of rare-earth valent state in γ'-irradiated CaF₂:Pr crystals by the eximer laser radiation: investigation and application

Svetlana G. Lukishova

Institute of Radioengineering & Electronics of the USSR Academy of Sciences, Prospekt Markska 18, 103907, Moscow, USSR

Aleksej Z. Obidin, Sergej K. Vartapetov, Igor A. Veselovsky, Anatoly V. Osiko, Tamara V. Tulajkova, Valery V. Ter-Mikirtychev

Institute of General Physics of the USSR Academy of Sciences, Vavilov Street 38, II7942, Moscow, USSR

Nestor Raul Minhuyê Mendez

Hospital Lima Peru, Avenue Brasilia 42, Lima, Peru

ABSTRACT

This paper presents a novel application of UV laser radiation: fabrication of soft or apodized apertures (AA) with smooth decreasing from centre to edges transmission profiles for high-power single-pulse visible and near IR lasers. Such units are used both outside and inside cavity for beam shaping, for avoiding hard-edge Fresnel diffraction ripples in laser amplifiers, for increasing the second harmonic conversion efficiency, for the brightness enhancement of master oscillators in single-mode lasing.

The method is easy and involves irradiating of pre γ'-colored (radiatively reduced) CaF₂ crystals doped with rare-eartns (TR) across a certain diameter by UV laser radiation.

The optical density of these crystals under the UV irradiation drops due to the photochemical changes of TR valent state (the photo-oxidation of TR²⁺ to TR³⁺ with stable bleaching).

The AA were made of CaF₂:Pr crystal with the use of 248nm and 308nm laser radiation. The transmission profiles of these AA are presented.

The kinetics of stable bleaching of γ’-irradiated CaF₂ crystals doped with both Pr and two rare earth activators (Pr, Nd) were investigated in beam of 308nm laser. The absorption spectra of these crystals before and after bleaching were obtained. All results have been compared with the case of 488nm argon laser irradiation.

An interesting phenomenon of coloration increasing in some CaF₂:Pr crystals instead of bleaching under 248nm laser irradiation has been observed. This coloration destroyed in beam of 308nm laser.

Some examples of application of the AA on the basis of photooxidation for beam shaping, 1.06μm second harmonic conversion efficiency increasing, and brightness enhancement of 1.06μm and 2.94μm oscillators.
are presented herein.

I. INTRODUCTION

The problem of fabrication of AA for high-power lasers with wavelengths $\lambda$ in near-IR demands the crystals with special composition: the induced absorption coefficient of these crystals under the irradiation by the ionizing radiation, $K$ must have a value greater than 1-2 cm$^{-1}$ in this spectral range. The induced absorption of such materials must be stable in near-IR laser beams.

The very good material for producing AA on the basis of bleaching of $\gamma$-irradiated crystals is fluoride (CaF$_2$) doped with rare-earths. Such crystals were found to be perspective for fabrication of AA up to 3.4 $\mu$m and also in the visible region. There were samples of CaF$_2$ with values of absorption coefficient $K$ ~ 1.8-6 cm$^{-1}$ at $\lambda$ = 1.06 $\mu$m.

Using of rare-earth activators is based on considerable difference of TR$^{3+}$ and TR$^{2+}$ absorption spectra in visible and near-IR region. The absorption spectra of TR$^{3+}$ in this range are caused by parity-forbidden $f$-$f'$-transitions inside the same electron configuration, these spectra consist of groups of narrow discrete lines. Allowed 4f-5d transitions with more wide absorption lines are known to be in the UV region of spectrum for the TR$^{3+}$ II. In spite of TR$^{2+}$ have the same electron configuration as corresponding TR$^{3+}$ (e.g., Sm$^{2+}$ has the following electron configuration: 4f$^5$5s$^2$5p$^6$, that is the same one for Eu$^{3+}$), 4f$^n$-5d-electron configurations of TR$^{2+}$ is located lower than in the case of TR$^{3+}$. That is why along with typical for the rare earths forbidden transitions inside 4f$^n$ configuration, the allowed ones in mixed 4f$^n$-5d configurations with wide intensive absorption bands in visible and near-IR region take place.

The typical valent state of rare-earths in the chemical compositions is known to be as +3. It should be mentioned that Ce, Pr, and Tb can have +4 valent state. In the CaF$_2$ lattice owing to divalent state of Ca, the possibility of change the rare-earth valent state from +3 to +2 enhances. The ordinary valent state of TR in grown CaF$_2$:TR is found to be as +3, but under the action of different external sources (e.g., irradiation by ionizing radiation, additive coloring in alkaline-earth vapour, electrolysis) the TR valent state can become +2. Heating up to 200-400°C and irradiation by light from visible to UV can change divalent state of TR on trivalent one $^{12}$.

In the set of TR the best one for doping in CaF$_2$ for fabrication of AA in near-IR spectral region is found to be praseodymium impurity: Pr$^{3+}$ has wide intensive absorption band in visible and near-IR, while Pr$^{2+}$ spectrum has few narrow lines. (It should be noted that in spite of in most papers, e.g., $^{9,10}$ these wide spectral bands identifies with bands of Pr$^{2+}$, there is also the opinion, that it may be a spectrum of Pr$^{4+}$ $^{9}$).

The typical spectrum of $\gamma$-irradiated CaF$_2$:TR crystals consists of
Summary of trivalent and divalent ions ones because of only 10% of \( \text{Tr}^{2+} \) convert to \( \text{Tr}^{2+} \) by \( \gamma' \)-irradiation. To have a pure \( \text{Tr}^{2+} \) spectrum in \( \text{CaF}_2 \) we must heat this crystal in alkaline-earth metal vapour (to carry out its additive coloration (thermochemical reduction)). Unfortunately, we don't know the examples of \( \text{CaF}_2 : \text{Pr} \) additive coloration, that is why we will consider the summary spectrum of \( \text{Pr}^{3+} \) narrow lines with the wide absorption bands after the \( \gamma' \)-irradiation of these crystals.

The phenomenon of photooxidation of \( \text{Tr}^{2+} \) in \( \text{CaF}_2 \) have been investigated in C, I2, I3, but the changes of \( \text{Pr} \) ions valent state under the light irradiation has not been considered. It should be also mentioned the paper I4 where some photochemical bleaching of pure \( \text{CaF}_2 \) without impurities colored by ionizing radiation has been investigated.

In this paper we consider the advantage of using the UV radiation as compared with visible light for the photooxidation and optical bleaching efficiency. The main difficulty for producing AA with "soft" transmission profile is following: creation the high-quality beam spot of UV source. For inside-cavity AA with diameter 2-4mm with the use of lens in beams of 308nm and 248nm lasers this problem has been solved.

2. Absorption Spectrum of \( \gamma' \)-Irradiated \( \text{CaF}_2 : \text{Pr} \) Crystals

\( \text{CaF}_2 \) single crystals doped with \( \text{PrF}_3 \) were grown by Stockbarger technique in the specific reactive atmosphere to be of necessity for the alkaline earth and rare earth fluoride crystals of good optical quality processing. The equipment used was in general outline like the one, described in 15. In a typical run a carbon crucible was filled with the mixture of the previously ground \( \text{CaF}_2 \) crystals "for an optical application" grade (purchased from the Industrial Branch of the State Optical Institute, Leningrad) and commercially available \( \text{PrF}_3 \) powder (better, than four nines pure with respect to cation). The \( \text{PrF}_3 \) concentration values ranged from 0.005 to 0.5 mol.%. The reactive atmosphere employed was obtained by thermal decomposition of teflon in vacuum or inert gas atmosphere just before melting the charge.

This method has yielded the crystals with good transparency in visible and near-IR region, absorption spectra demonstrating only characteristic \( \text{Pr}^{3+} \) ions lines. Figure 1 presents the absorption spectrum of one of such crystals with \( \text{Pr} \) concentration 0.2mol.% and sample thickness \( d=7 \text{mm} \) (curve 1, solid line).

Curve 2 at Figure 1 demonstrates the absorption spectrum of this crystal after the exposition of \( \gamma' \)-irradiation (10⁸ roentgen).

Curves 3 and 4 (dotted lines) at Figure 1 present absorption spectra of pure \( \text{CaF}_2 \) with \( d=7 \text{mm} \) before the \( \gamma' \)-irradiation and after it accordingly. In difference of paper 14 the value of irradiation dose in our case was greater (10⁹ roentgen), that is why the induced absor-
ption coefficients $K$ are found to be greater in our experiments than in paper I.

It should be mentioned that at first stage of $\gamma$-irradiation the $\text{TR}^{2+}$ concentration grows very quickly with dose increasing. In the case than irradiation dose value exceed $3 \times 10^8$ roentgen the $\text{TR}^{2+}$ concentration enhances slowly. Interesting that in Pr concentration range in CaF$_2$ crystals from 0.1 - 0.6 mol.% the absorption coefficients after irradiation don't depend on the value of concentration.

![Graph](image)

Figure 1.

The measurements at Figure 1 were made with the use of Spectrophotometers SF-8, SF-20 of LOHO (Leningrad), Spectrometer Lambda 9 of Perkin Elmer Ltd., IKS-29 of LOHO, model Graphics Ix of Perkin Elmer Ltd. Spectrophotometers.

3. OPTICAL BLEACHING OF $\gamma$-COLORED CaF$_2$:Pr CRYSTALS UNDER THE IRRADIATION OF SHORT WAVELENGTH LIGHT

3.1. UV light irradiation

Figure 2 presents the photograph of CaF$_2$:Pr AA with $\approx 10$mm in diameter made with the use of 1kW mercury lamp LKSSH-1000 with water filter to cut of thermal radiation. The irradiation time was $\approx 10$ hours when we used lens to focus lamp radiation.

![Image](image)

At the length of crystal 25mm with irradiation of each of two polish crystal faces we obtained greater than 10$^3$ times bleaching (in transmittance values) for $\lambda = 0.63 \mu m$, and $\approx 160$ at $\lambda = 1.06 \mu m$ at above mentioned time interval.

To investigate bleaching of crystals under 308nm XeCl laser light irradiation we used 1mm thickness 3' samples.

Figure 2.

Figure 3 presents the kinetics of bleaching of two of such samples: curve 1 - for CaF$_2$:Pr crystal with Pr concentration $\approx 0.6$ mol.%, and curve 2 - for CaF$_2$-0.2rF$_3$:0.05NdF$_3$ sample. ELI-73 of Tartu EAR A8ESSR had 20mJ 25ns pulses with 10Hz repetition rate. The beam spot had 5x10$^3$mm sizes.

Figure 4 shows the changes of spectra in these experiments: solid lines- before 308nm irradiation, and dotted lines-after above mentioned expositions.
An interesting effect has been observed in one of CaF$_2$:Pr sample (Pr concentration was $\sim 0.2\text{mol.\%}$, and sample was cut from the 200mm crystal of State Optical Institute growth). The 30" polish sample with 38mm thickness after $10^4$-$10^5$rad $\gamma$-radiation dose was exposed by 248nm KrF laser radiation during 15min (15ns 1Hz repetition rate discharge laser had pulse energy $E \approx 50$nmJ with $0.7 \times 1.2$cm$^2$ beam spot). Instead of bleaching which we observed with another CaF$_2$:Pr samples under 248nm light radiation, the additional induced absorption appeared in $\sim 5$-10mm layer inside of such crystal. Figure 5 shows the changes in absorption spectrum of this sample (curve 1-before 248nm irradiation, curve 2-after it).

After the exposition of such crystal sample by 308nm radiation (discharge XeCl with 15ns pulse duration, 1Hz repetition rate and $E = 30$nmJ in $0.9 \times 0.6$cm$^2$ spot) during 15 min the absorption induced by 248 nm radiation disappeared.

3.2. Fabrication of apodized apertures by the eximer laser radiation

In described below experiments we used 5mm thickness CaF$_2$-0.2PrF$_3$ samples after five years ago irradiation by $10^7$roentgen dose $\gamma$-radiation.

Three schemes of irradiation by eximer laser light are presented at Figure 6a,b,c.
Figure 6. AA fabrication by eximer laser light.

AA transmission profiles are presented at Figure 7. To increase the transmittance value in the central part of AA we must expose crystals by laser irradiation in longer time interval. It should be noted that the problem of maximum transmittance in the centre after the bleaching must be considered in special investigations.

As compared with 488nm argon laser radiation the efficiency of bleaching in the case of 485nm is less than in UV region. The same values of transmittance in the centre of these crystals we observed only after 2-3 hours 2W power continuous laser irradiation. The heating of crystal during argon light irradiation with this power can cause in crystal undesirable stresses. To be fair it is easier to make accurate profile of AA with good optical quality commercial argon laser beams than in eximer ones.

4. APPLICATION IN NEAR-IR LASERS OF APODIZED APERTURES ON THE BASIS OF PHOTOOXIDATION

Note that at λ=1.06μm under the irradiation of single-pulse laser radiation these AA made of γ-irradiated CaF2:Pr crystals do not bleach till samples are damage. In focused laser beam at λ=1.06μm the surface damage of these crystals is observed at the intensity of 5.10^9 W/cm^2, bulk damage at 2.10^11 W/cm^2 (pulse duration was 10ns, beam spot in focus was 27μm and 4.6μm, respectively).

AA were used inside the cavity of 2.94μm Er:YAG laser in free running oscillation and Q-switched 1.06μm Nd:YAG laser.

Er:YAG laser had a semiconfocal resonator with 3m hard mirror and 30% reflectance plane one. In case of hard-edge aperture inside this resonator it must have a diameter less than 3mm for single-mode lasing. 1.3-1.8 times increasing in output energy (at different pumping voltage) and 1.52 times diminishing in beam divergence in single-mode lasing as compared with hard-edge aperture have been observed in
case of photooxidation AA inside resonator.

A single-mode lasing of Nd:YAG oscillator with 8% reflectance and hard plane mirrors took place only with 2.5mm hard-edge aperture with about 30% of the output energy hard aperture being removed. When we placed AA the output energy in a single-mode lasing increased up to 55%(0.1J) from the multimode case. The detail information of these experiments is in the paper.

AA of Figure 2 has been used for 2 years at laser system output of 2.5J energy and 25ns single pulse duration(λ=1.06μm). In this case second harmonic conversion efficiency increased from 40% up to 55% owing to better filling the cross-section(AA has smooth flat-top transmission profile). Such experiment has been made by Yu.K.Nizienko of the I.V.Kurchatov Institute of Atomic Energy.

5. CONCLUSIONS

The investigations shown that fabrication of photooxidation AA with optical bleaching by the eximer laser radiation is easy and fast. The efficiency of bleaching in the case of UV radiation is greater than in visible range of spectrum. Two problems must be solved to produce commercial AA: 1) to make the transmittance in the centre of AA $\sim$ 94%, and 2) to shape high-quality eximer laser beams for fabrication the AA with large diameter(up to 50mm).

6. ACKNOWLEDGMENTS

The authors express their gratitude, to V.A.Sokolov, E.A. Simun, V.K.Karpovich of the State Optical Institute for fabricating of some CaF$_2$:Pr samples, V.A.Konjushkin of General Physics Institute for the possibility given to us to irradiate the crystals by γ-radiation, A.A. Nesterenko and G.P.Kuzmin of General Physics Institute for help in irradiation of crystals on ELI-73 eximer laser.

7. REFERENCES


