

# Fluorescent Aluminum Oxide Crystals for Volumetric Optical Data Storage and Imaging Applications

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New fluorescent aluminum oxide crystals ( $\text{Al}_2\text{O}_3\text{:C,Mg}$ ) for volumetric optical data storage and imaging applications were investigated. Magnesium impurity and double oxygen vacancy aggregate defects are responsible for the main optical properties of the new material. Spectroscopic investigation of these defects in different charge states was performed. Optical absorption, excitation-emission spectra and fluorescent lifetime of the new fluorescent medium were studied. Quantum yield of fluorescence from  $\text{Al}_2\text{O}_3\text{:C,Mg}$  crystals was measured in comparison with standard laser dyes.

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**KEY WORDS:** Fluorescence; optical absorption; aluminum oxide crystals; Mg impurity.

## INTRODUCTION

Corundum or sapphire ( $\alpha\text{-Al}_2\text{O}_3$ ) is an important technological material in many optical and electronic applications. Chromium doped sapphire (ruby) was the crystal used for the first solid state laser.  $\text{Al}_2\text{O}_3$  doped with carbon was successfully used as a supersensitive luminescent detector of radiation [1,2]. Recently  $\text{Al}_2\text{O}_3\text{:C,Mg}$  was suggested as a fluorescent medium for optical data storage [3,4]. For efficient data storage, it is necessary, that  $\text{Al}_2\text{O}_3$  crystals contain both a high concentration of recombination-luminescence centers and defects capable of trapping electrons. Crystal growth in a highly reducing atmosphere made it possible to create effective luminescent centers (oxygen vacancies in the form of F-centers), thus making  $\text{Al}_2\text{O}_3$  suitable for different luminescence applications.

The nature and the properties of point defects (color centers) in  $\alpha\text{-Al}_2\text{O}_3$  crystals, either undoped, or doped with Mg, have been the subject of several studies [5–9]. It was shown that numerous optical absorption bands may be induced in  $\alpha\text{-Al}_2\text{O}_3$  by neutron, proton, or electron irradiation and ion-implantation methods. Some of these ab-

sorption bands were assigned to specific point defects. The 205 nm (6.05 eV) band was identified as an F-center (an oxygen vacancy with two electrons). The 230 nm (5.4 eV) and 255 nm (4.8 eV) bands were assigned to an  $\text{F}^+$ -center (an oxygen vacancy with one electron). Single oxygen vacancy defects can also be produced by thermochemical reduction, additive, or subtractive coloration.

Some progress was made identifying oxygen aggregate vacancies with the many bands that appear following exposure to high energy particles. For example, according to Evans et al. [6] three absorption bands in fast neutron irradiated  $\alpha\text{-Al}_2\text{O}_3$  are located at 303 nm (4.09 eV), 357 nm (3.47 eV) and 450 nm (2.75 eV). These bands were assigned to  $\text{F}_2^-$ ,  $\text{F}_2^+$  and  $\text{F}_2^{2+}$ -centers respectively and they represent different charge states of the same  $\text{F}_2$ -type defect (a cluster of two oxygen vacancies).

It is important to note, that all previous studies were done on  $\alpha\text{-Al}_2\text{O}_3$  crystalline material, where oxygen vacancies were induced as a result of exposure to energetic particles, or on magnesium-doped  $\alpha\text{-Al}_2\text{O}_3$  without a high concentration of oxygen vacancies. In this paper we present the properties of a new material—aluminum oxide crystals doped with carbon and magnesium and having a high concentration of aggregate oxygen vacancy defects ( $\text{Al}_2\text{O}_3\text{:C, Mg}$ ). This material, due to the presence of different luminescent centers, is very promising for applications in optical data storage and imaging [3,4].

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## SAMPLES AND EXPERIMENTAL PROCEDURES

The  $\text{Al}_2\text{O}_3\text{:C,Mg}$  crystals doped with a combination of carbon and magnesium impurities were grown using the Czochralski method with a seed orientation along the optical  $c$ -axis. The crystal growth process was performed in a highly reducing atmosphere with a low partial pressure of oxygen that is needed for the formation of oxygen vacancies in the  $\text{Al}_2\text{O}_3$  crystal structure.

Samples for optical absorption and fluorescent measurements with a known crystallographic orientation were cut and polished to different sizes and shapes. Plates of  $2 \times 10 \times 14$  mm and parallelepiped of  $8 \times 8 \times 13$  mm were used. Optical absorption (OA) measurements were performed using a UV-2401 PC Shimadzu spectrophotometer.

Excitation-emission spectra were obtained using a fluorimeter constructed from two Acton Research scanning spectrographs. One of them was equipped with a thermoelectrically cooled Princeton Instruments CCD camera. Deuterium (30 W), halogen (150 W), and xenon flash (20 W) lamps were used as excitation sources. The emitted light was collected at  $90^\circ$  to the excitation beam. Anisotropy of OA and fluorescence were measured by the insertion of dye type UV polarizers into the appropriate light paths.

Photochromic transformations in the crystals were performed using a Continuum Panther Optical Parametric Oscillator (OPO) pumped with the 355 nm, third harmonic of Nd:YAG laser. The OPO was tuned either to 435 nm or 335 nm wavelength with laser pulses having 4.5 ns half-width, and a peak power of up to  $300 \text{ MW/cm}^2$  was used to perform photochromic transformation of color centers in  $\text{Al}_2\text{O}_3\text{:C,Mg}$  crystals. It was also shown that a similar photochromic transformation can be achieved in a tightly focused CW laser beam of blue (405 nm) semiconductor lasers.

Fluorescence lifetime was measured using a fast (5 GS/s) Tektronix TDS-3052 digital oscilloscope connected to a ThorLabs DET-210 photodiode having DC to 1 GHz bandwidth. Fluorescence from the sample was excited either by 60 ps pulses from a 411 nm PicoQuant diode laser or using attenuated 4.5 ns laser pulses generated by the OPO tuned to an appropriate wavelength. The emitted light was separated from the excitation light by using appropriate band-pass glass filters.

Measurements of fluorescent quantum yield were performed using two experimental setups: one was the fluorimeter described above and the other was constructed using a Melles Griot He-Cd 70 mW, 442 nm laser, imaging optics, and Si photodiodes. All measurements were corrected to appropriate irradiance of the light sources,

wavelength-dependence of the efficiencies of the gratings, the photodiodes, and the CCD. The measurements were performed for several orientations of  $\text{Al}_2\text{O}_3\text{:C,Mg}$  crystals and standard laser dyes: fluorescein and coumarin-153 with known quantum yields of fluorescence [10,11].

## EXPERIMENTAL RESULTS

### Optical Absorption

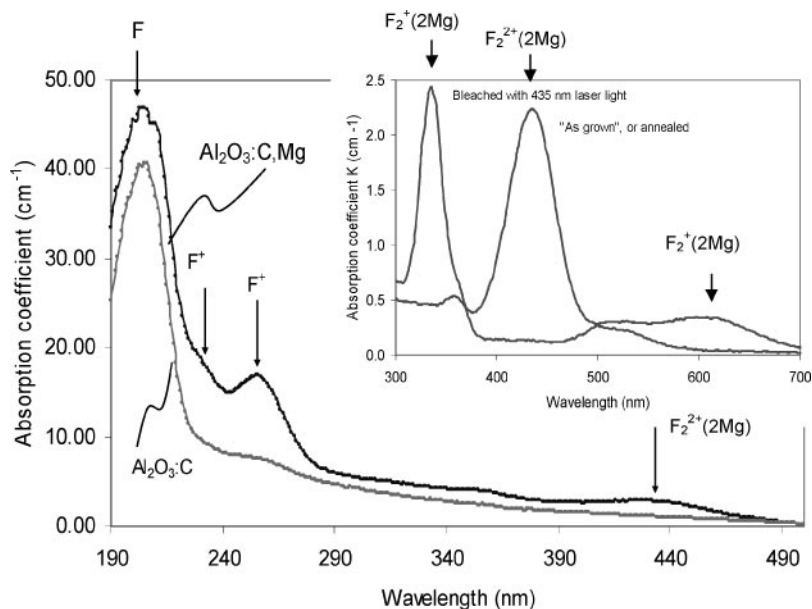
Typical optical absorption spectrum of  $\text{Al}_2\text{O}_3\text{:C,Mg}$  is shown in Figure 1. The band at 205 nm (6.05 eV) is assigned to F-centers and the band at 255 nm is attributed to  $\text{F}^+$ -centers [5,6]. Unlike in  $\text{Al}_2\text{O}_3$  crystals, undoped or doped purely with carbon, a new absorption band at 435 nm (2.85 eV) appears in Mg-doped crystals. Due to the absorption in the blue region (at 435 nm),  $\text{Al}_2\text{O}_3\text{:C,Mg}$  crystals have yellow-green coloration. This coloration is stable when illuminating the crystal with incandescent light or CW 442 nm laser light of He-Cd laser. These very stable color centers can be destroyed only by heating the crystal above  $700^\circ\text{C}$ .

Thermal instability of the color centers responsible for the 435 nm absorption band is an indication that these centers are complex aggregate centers that dissociate during high temperature annealing. A short annealing time is needed for the destruction of the coloration. On the contrary, the absorption of F and  $\text{F}^+$ -centers does not change during annealing even up to  $1200^\circ\text{C}$ . These facts allow one to speculate that this thermally activated process of discoloration is not a result of oxygen diffusion into the bulk of the crystal but is merely a dissociation of aggregate defects.

Photochromic transformation of color centers in  $\text{Al}_2\text{O}_3\text{:C,Mg}$  crystals can be performed using a high peak power pulsed laser illumination with a wavelength corresponding to particular absorption bands. After illuminating the crystal with pulsed 435 nm laser light (bleaching procedure) green coloration and 435 nm OA band disappear, and new OA bands at 335, 520, and 620 nm show up (see Fig. 1, insert). Partial reverse photochromic transformation can be achieved by illuminating the crystal with pulsed 335, or 620 nm laser light.

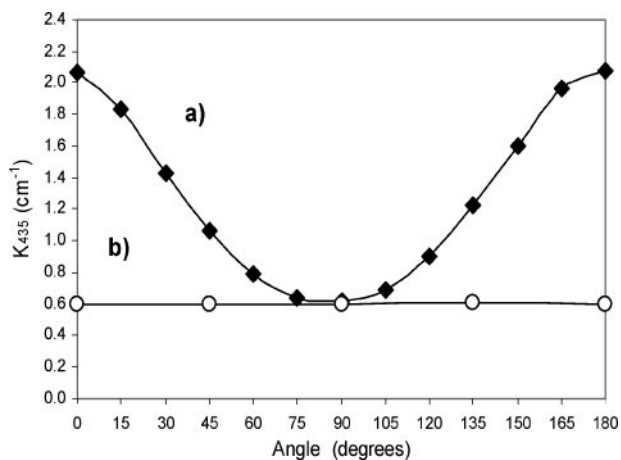
### Anisotropy of Optical Absorption

Studies of optical absorption anisotropy can give a clue to the possible origin of the defects responsible for the observed absorption bands. The three main absorption bands, which were discussed above (at 335, 435, and 620 nm), show rather strong anisotropy. Figure 2 shows



**Fig. 1.** Optical absorption bands in  $\text{Al}_2\text{O}_3:\text{C}$  and  $\text{Al}_2\text{O}_3:\text{C,Mg}$  crystals. The insert shows the photochromic transformation of  $\text{Al}_2\text{O}_3:\text{C,Mg}$  under 435 nm pulsed laser light.

dependence of the optical absorption coefficient for the 435 nm band on the angle between the optical  $c$ -axis of the crystal and the direction of polarization of light in the spectrophotometer. When light propagates perpendicular to  $c$ -axis ( $c \perp k$ ) rotation of the crystal around  $k$ -vector direction causes strong changes in the coefficient of absorption. The absorption coefficient varies from  $K_{\parallel} = 2.07 \text{ cm}^{-1}$ , when  $c$ -axis of the crystal is parallel to the polarization direction ( $c \parallel E$ ), down to  $K_{\perp} = 0.613 \text{ cm}^{-1}$ , when  $c$ -axis is perpen-



**Fig. 2.** Angular dependences of the 435 nm OA band for different polarization directions: (a)  $c \perp k$  and (b)  $c \parallel k$ .

dicular to the polarization direction ( $c \perp E$ ). The observed anisotropy of the 435 nm band  $A = K_{\parallel}/K_{\perp} = 3.38$ .

When light propagates parallel to the  $c$ -axis of the crystal ( $c \parallel k$ ), rotation of the sample under polarized light does not change the absorption coefficient (Figure 2, curve b). It remains equal to  $0.613 \text{ cm}^{-1}$  at all angles of rotation and is the same as the absorption coefficient for the geometry when light propagates perpendicular to the plane of  $c$ -axis and polarization direction is perpendicular to  $c$ -axis (Figure 2, curve a).

Angular dependences of the absorption coefficients for the 335 and 620 nm bands are similar to the dependence obtained for the 435 nm band, though these anisotropy coefficients are lower (see Table I). The close values of anisotropy coefficients for the 335 and 620 nm bands (2.40 and 2.43, respectively) may suggest that both bands belong to the same aggregate defect with the same charge state.

### Excitation-Emission Spectra

Excitation-emission (EE) spectra allow one to better distinguish between different types of color centers because, unlike OA spectra, EE spectra give one two-dimensional information and show separate centers with overlapping OA bands. EE spectra were obtained for two states of  $\text{Al}_2\text{O}_3:\text{C,Mg}$  crystal: (a) for an "as grown" or annealed ("erased") state and (b) for a bleached (or "written")

**Table I.** Anisotropy of Optical Absorption Bands in  $\text{Al}_2\text{O}_3:\text{C,Mg}$  Crystals

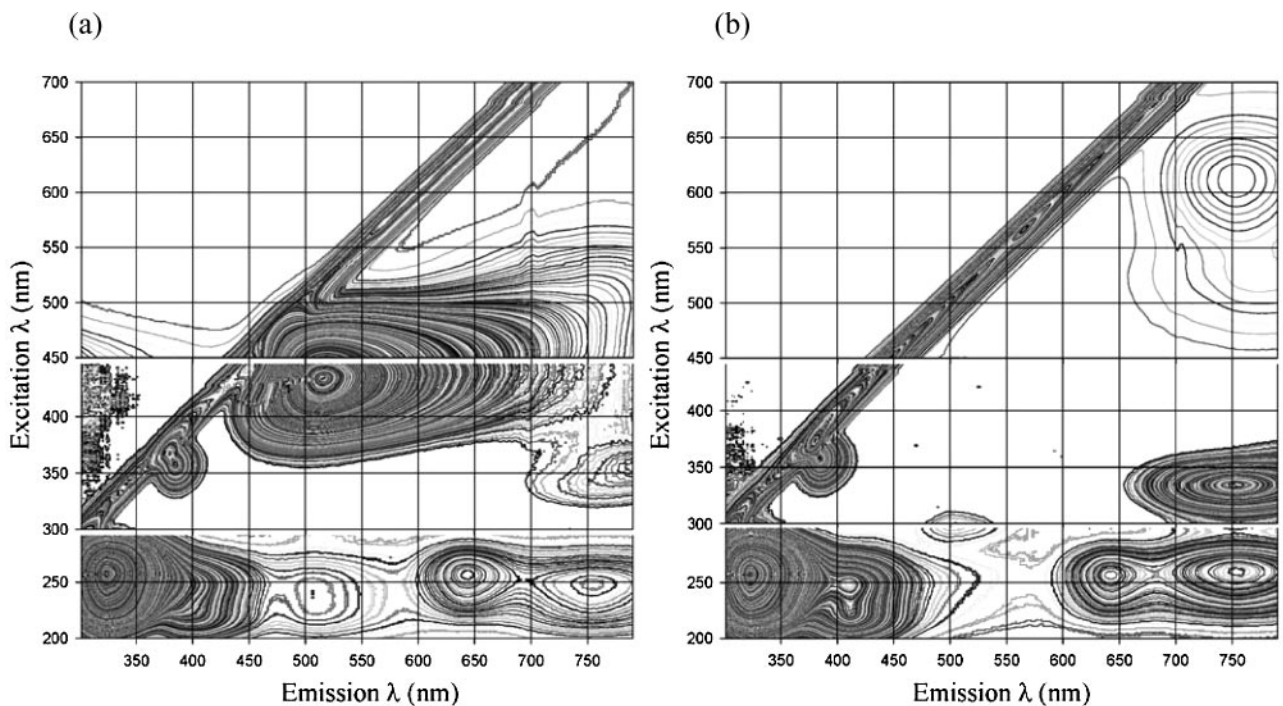
OA band	Sample treatment	$K_{\parallel}$ ( $\text{cm}^{-1}$ )	$K_{\perp}$ ( $\text{cm}^{-1}$ )	Anisotropy of absorption $A = K_{\parallel}/K_{\perp}$
435 nm (2.85 eV)	“As grown” or annealed at 670°C	2.070	0.613	3.38
335 nm (3.70 eV)	Bleached with 435 nm laser light	0.968	0.404	2.40
620 nm (2.00 eV)	Bleached with 435 nm laser light and annealed at 350°C	0.051	0.021	2.43

state (Fig. 3). The bleaching was performed as described above with 435 nm pulsed laser light from the OPO.

Several of excitation-emission bands are well known from the literature and were identified. Single oxygen vacancy centers like F- and  $\text{F}^+$ -centers were studied extensively [5,6] and have well identified excitation-emission bands. F-centers show strong absorption at 205 nm and emit light at 420 nm.  $\text{F}^+$ -centers exhibit characteristic absorption-excitation bands at 230 and 255 nm with emission at 330 nm. The 230 nm absorption-excitation band because of a strong anisotropy can be seen only at a certain orientation of the crystal when  $c \parallel k$ . Among double oxygen vacancy centers cited in the literature neutral  $\text{F}_2$ -centers with an absorption-excitation band at 358 nm and an emission band at 380 nm were identified. Another known color

center,  $\text{F}_2^+$ -center, shows absorption at 302 nm and emission at 515 nm.

Introduction of Mg-impurity stimulates creation of several new color centers needed for charge compensation of  $\text{Mg}^{2+}$ -ion which become negatively charged with respect to the lattice when it substitutes for  $\text{Al}^{3+}$ -ion. These new color centers were not previously (at least to our knowledge) described in the literature. Absorption-excitation band at 435 nm with the corresponding emission band at 520 nm is characteristic to “as grown” or annealed to 670°C crystal. After 435 nm pulsed laser illumination, the 435 nm band disappears and two other absorption-excitation bands at 335 and 620 nm with a corresponding emission band at 750 nm show up as a result of a photochromic transformation. Excitation-absorption



**Fig. 3.** Excitation-emission spectra for  $\text{Al}_2\text{O}_3:\text{C,Mg}$  crystal in different states: (a) “as grown” or annealed to 670°C and (b) bleached with 435 nm pulsed laser light.

band centered at 520 nm with an associated emission at 770 nm also undergo some changes during illumination and annealing but they are not so easy to explain. EE bands at 255/660 nm and 360/780 nm are the result of a 2<sup>nd</sup>-order diffraction of 255/330 nm and 360/380 nm bands respectively.

### Fluorescence Lifetime

Fluorescence lifetime is another parameter that helps to identify a color center. For example, F-centers have a characteristic long lifetime equal to 35 ms due to the forbidden triplet-singlet transition [6], whereas F<sup>+</sup>-center has an extremely short lifetime that is less than 7 ns [5]. In our experiments F<sup>+</sup>-center luminescence at 330 nm excited by 255 nm light was shorter than the 4.5 ns half-width of the laser pulse. The lifetime of the 520 nm fluorescence under excitation into a 435 nm absorption-excitation band characteristic to “as grown” or thermally annealed crystals was measured using the experimental setup described above. A blue laser producing 60 ps, 411 nm excitation pulses at 20 MHz was used. Fluorescence decay waveforms were obtained from the oscilloscope (Fig. 4). Fitting the waveforms with the single exponential function gave the decay constant equal to  $9 \pm 3$  ns.

The crystal in a “written” state obtained by bleaching it with a 435 nm pulsed laser light from the Panther OPO showed 750 nm near IR fluorescence. This fluores-

cence can be excited by stimulating one of the absorption-excitation bands centered at 260, 335, and 620 nm. The study of the 750 nm fluorescence showed that it has a much longer lifetime of  $80 \pm 5$  ns (Fig. 5) and it can be measured with the stimulation of 4.5 ns pulses from the OPO tuned to an appropriate absorption band.

### Quantum Yield and Anisotropy of Fluorescence

Results of the fluorescence quantum yield measurements obtained for a different orientation of the optical *c*-axis of the crystal with respect to the direction of light propagation and its polarization are presented in Table II. All data were normalized to the quantum yield of standard organic dyes: fluorescein and coumarin-153 equal to 0.925 and 0.380 respectively [10,11]. Generally, the relative quantum yield is determined by comparison of the wavelength-integrated intensity of the unknown sample, *x*, to that of the standard sample, *s*:

$$Q_x = Q_s(A_s/A_x)(\lambda_s/\lambda_x)(F_x/F_s)(n_x/n_s)^2 \quad (1)$$

where *A* is the absorbance at the excitation wavelength  $\lambda$ , *F* is the area under the corrected emission curve, and *n* is the refractive index.

As one can see from the Table II Al<sub>2</sub>O<sub>3</sub>:C,Mg crystals have a very high quantum yield. It is also apparent from the presented data that the fluorescence is strongly anisotropic

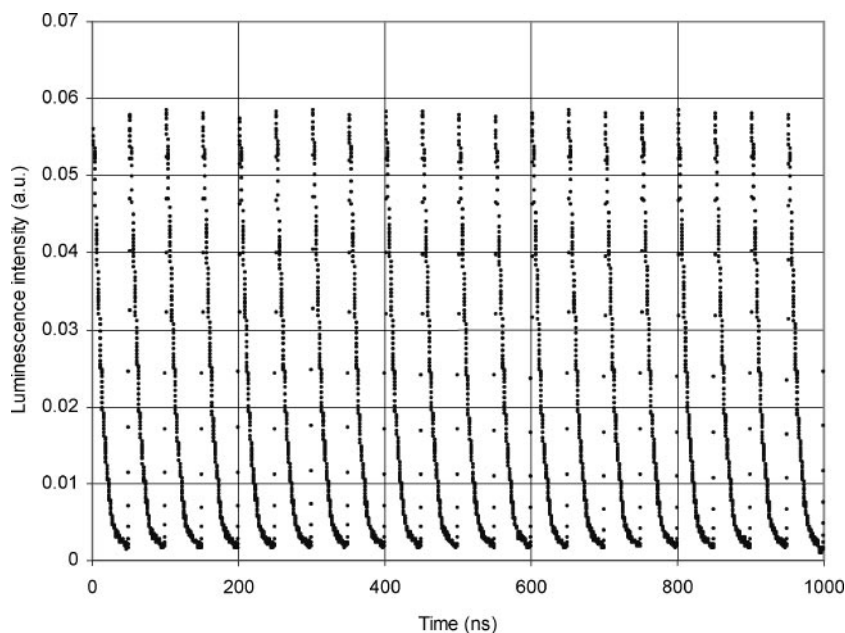


Fig. 4. Readout of 520 nm fluorescent signal with 20 MHz excitation pulses of 411 nm laser showing a F<sub>2</sub><sup>+</sup>(2Mg)-center lifetime of 9 ns.

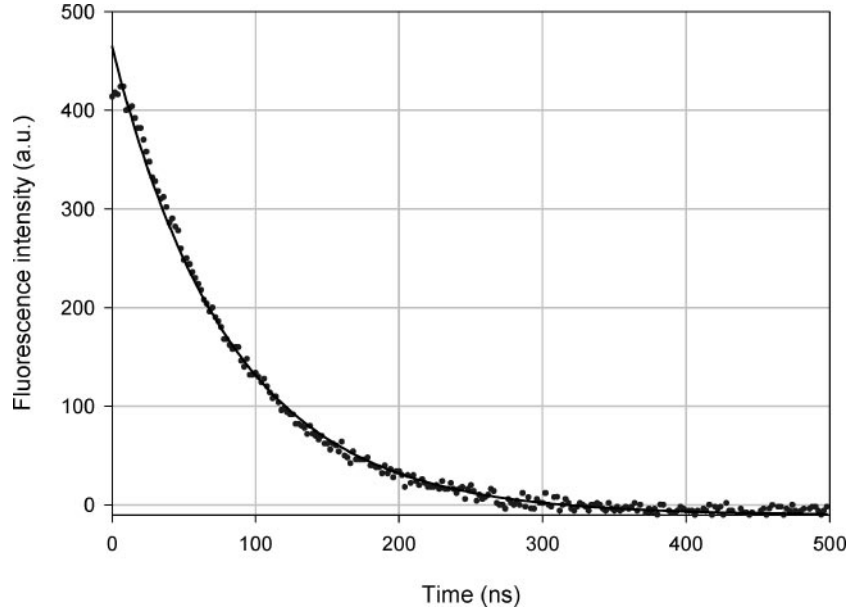


Fig. 5. Decay of fluorescence of near-IR emission at 750 nm with lifetime equal to 80 ns.

with the highest yield taking place when  $k$ -vector is parallel to the optical  $c$ -axis of the crystal and the fluorescence is measured perpendicular to this direction. To determine the average quantum yield of  $\text{Al}_2\text{O}_3$  crystal more measurements need to be performed for other combinations of the crystal optical axis orientation, light propagation direction, and emission measurement direction.

#### DISCUSSION: ELECTRONIC PROCESSES IN $\text{Al}_2\text{O}_3\text{:C,Mg}$ CRYSTALS

$\alpha$ - $\text{Al}_2\text{O}_3$  has a rigid, slightly distorted hexagonal-close-packed  $\text{O}^{2-}$  sub-lattice with  $\text{Al}^{3+}$  ions occupying two out of every three octahedral interstices. Each  $\text{O}^{2-}$ -ion is surrounded by four tetrahedral nearest-neighbor  $\text{Al}^{3+}$ -

ions. Crystal growth in a highly reducing atmosphere stimulates production of oxygen vacancy defects that were identified using OA and excitation-emission spectroscopy. The OA band centered at 205 nm with the corresponding emission at 420 nm is assigned to F-centers. The 230 and 255 nm bands with the emission at 330 nm are assigned to  $\text{F}^+$ -centers, and their production is stimulated by the presence of  $\text{Mg}^{2+}$ -ions substituting  $\text{Al}^{3+}$ -ions in the lattice of  $\text{Al}_2\text{O}_3$ . These data is well supported by known literature [5–9].

At certain crystal growth conditions new color centers were produced in the lattice of  $\text{Al}_2\text{O}_3\text{:C,Mg}$  crystal, and they are attributed to the creation of the double oxygen vacancy defects as a result of aggregation of single vacancy defects. The 435 nm absorption band with the corresponding emission at 520 nm and 9 ns lifetime is assigned to the  $\text{F}_2^{2+}(2\text{Mg})$ -centers, similar to  $\text{F}_2^{2+}$ -centers in

Table II. Measurements and Calculations of Fluorescence Quantum Yield for  $\text{Al}_2\text{O}_3\text{:C,Mg}$  in Comparison with Standard Laser Dyes: Fluorescein [10] and Coumarin-153 [11]

Sample	$K$ ( $\text{cm}^{-1}$ ) at 442 nm	Fluorescence under He-Cd laser excitation (a.u.)	Fluorimeter Emission area (a.u.)	Quantum Yield [Ref.]	Quantum Yield (vs. Fluorescein in NaOH)		Quantum Yield (vs. Coumarin-153 in ethanol)	
					He-Cd laser	Fluorimeter	He-Cd laser	Fluorimeter
Fluorescein in NaOH	1.677	2.710	9.77	0.925 [10]	0.925	0.925	0.949	0.941
Coumarin-153 in ethanol	3.471	2.145	7.80	0.380 [11]	0.370	0.374	0.380	0.380
$\text{Al}_2\text{O}_3\text{:C,Mg}$ ( $c\parallel E$ )	2.070	2.003	7.68		1.015	1.078	1.041	1.097
$\text{Al}_2\text{O}_3\text{:C,Mg}$ ( $c\perp E$ )	0.613	0.407	1.53		0.696	0.726	0.714	0.739
$\text{Al}_2\text{O}_3\text{:C,Mg}$ ( $c\parallel k$ )	0.613	1.236	4.60		2.114	2.180	2.169	2.217

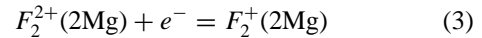
non-doped aluminum oxide irradiated with fast neutrons [6]. In comparison with simple  $F_2^{2+}$ -centers,  $F_2^{2+}(2Mg)$ -centers have a significant blue shift in the OA (435 nm vs. 459 nm) and the emission band (520 nm vs. 563 nm). Anisotropy of OA at 435 nm equals to  $A = K_{\parallel}/K_{\perp} = 3.38$  and relates to the angle of the dipole inclination  $\theta$  with respect to the  $c$ -axis through the expression [6]:

$$A = 2 \cot^2 \theta \quad (2)$$

The angle  $\theta$  obtained from the anisotropy data for the  $F_2^{2+}(2Mg)$ -center equals to  $38^\circ$ . That is exactly the same angle which was obtained for the  $F_2^{2+}$ -center created in  $Al_2O_3$  under neutron irradiation [6]. For the perfect  $Al_2O_3$  lattice the angle between two oxygen atoms located in adjacent basal planes is equal to  $33^\circ$ . We assume that the  $F_2^{2+}(2Mg)$ -center is a cluster of oxygen vacancies formed by two  $F^+$ -centers and charge-compensated by two Mg-impurity atoms (Fig. 6). Because of the complex nature of this cluster, they can be referred to as “aggregate” defects.

Optical absorption spectrum of  $Al_2O_3:C,Mg$  alters dramatically after exposure to 435 nm pulsed laser light (shown in the insert of Fig. 1). This procedure is called “bleaching,” because it results in the disappearance of 435 nm absorption band and in the loss of green coloration of the crystals. Instead of the 435 nm band, other absorption bands appear, the one at 335 nm being the most pronounced. The second absorption band appears at 620 nm. Both of these bands coincide with the excitation bands producing 750 nm emission and having  $80 \pm 5$  ns lifetime. In addition, the same emission at 750 nm can be excited with a 260 nm light. The latter excitation band can be either a third excited state of an electron center having an excited state split by a crystalline field or is a result of energy transfer between the  $F^+$ -center and this new aggregate center under study. We assign this center obtained by bleaching procedure to  $F_2^+(2Mg)$ -center—a three-electron center, which is a product of its conversion from  $F_2^{2+}(2Mg)$ -center according to the following

reaction:



where  $e^-$  is an electron released from another  $F_2^{2+}(2Mg)$ -center during the two-photon absorption/ionization process. The  $F_2^+(2Mg)$ -center can be also referred to as an aggregate defect, and it is similar in properties to  $F_2^+$ -center created by neutron irradiation and having 356 nm absorption and 380 nm emission [6].

It was assumed that the 335 nm and the 620 nm bands belong to the same defect because both bands have a similar anisotropy of their optical absorption  $A = K_{\parallel}/K_{\perp}$  equal to 2.40 and 2.43 respectively (see Table I).

Quantum yield of fluorescence was investigated so far only for the 435 nm excitation-520 nm emission band, and it was compared with the well known organic laser dyes fluorescein and coumarin-153. The results presented in Table II show both a very high fluorescence yield and its strong anisotropy for different combinations of the direction of light propagation, and the polarization direction with respect to the optical  $c$ -axis of the crystal. Full description of this study will be published later. Though, one main conclusion can be already made at this point:  $Al_2O_3:C,Mg$  has an extremely high average for all directions quantum yield of fluorescence close to 1.0.

$Al_2O_3:C,Mg$  is suggested as an efficient fluorescent two-photon medium [3,4]. The electronic processes which occur in the medium during “write” and “read” operations are explained using a band diagram in Fig. 7. Data storage media generally exist in at least two stable physical states assigned correspondingly to the logical “0” and “1” states. An initial configuration (logical “0” state) of “as-received” or “erased”  $Al_2O_3$  medium has a high concentration of  $F_2^{2+}(2Mg)$ -centers, characterized by the intensive absorption band centered at 435 nm.

By illuminating the medium with the “writing” laser light having a wavelength within 435 nm absorption band and intensity, which is high enough to perform sequential two-photon absorption and ionization of the defects, one may produce free electrons to be trapped in pre-existing electronic defects. The traps in  $Al_2O_3:C,Mg$  are deep enough to keep the charge carriers for a long time at an ambient temperature without being thermally released. This second state of the quantum system is now in a meta-stable (“charged”) configuration (logical “1” state). To “read” this state of the medium, stimulation light of the same, or different wavelength is applied and fluorescent photons are detected. In case of fluorescence one-bit recording, a “written” bit produces a reduced fluorescence intensity whereas an “unwritten” spot produces the original more intense fluorescence.

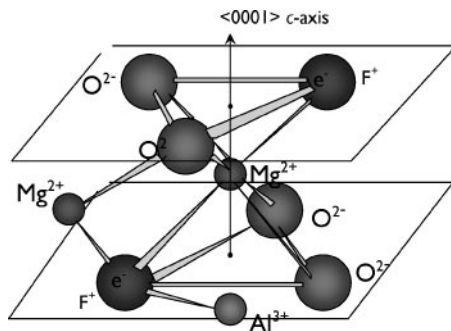
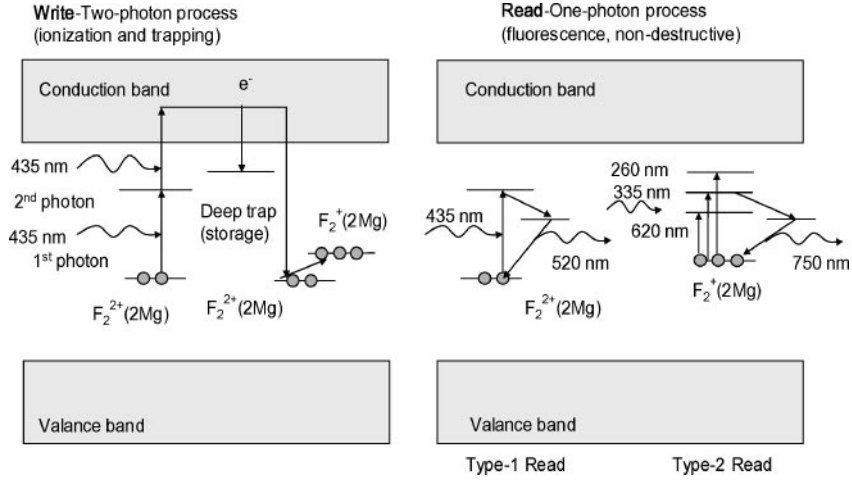


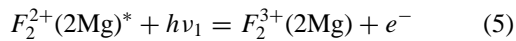
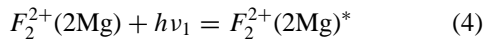
Fig. 6. Model of  $F_2^+(2Mg)$  aggregate defect.



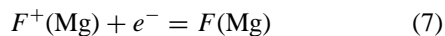
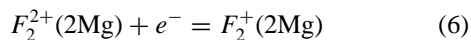
**Fig. 7.** Band diagram and electronic processes in  $\text{Al}_2\text{O}_3:\text{C,Mg}$  under laser light during “write” and “read” of optical data.

Electronic defects in wide gap dielectrics like  $\text{Al}_2\text{O}_3$  are characterized by energy levels of their ground and excited states. If the excited state of the electronic defect is located close to or within the conduction band, the defect may be ionized by one-photon absorption. A different situation takes place when the excited state is located deep within the energy gap of the crystal. Absorption of one photon corresponding to the energy transition between the ground and the excited states of an electronic defect, results in a localized transition followed by a non-radiative and a radiative decay (fluorescence). This one-photon absorption process is nondestructive and may be used for reading information repetitively.

“Writing” the data may be performed using sequential two-photon absorption [3] of  $435 \pm 40$  nm blue laser light utilizing the  $\text{F}_2^{2+}(\text{2Mg})$ -centers as described above. The first photon transfers one of the two electrons localized on the center to its excited state while the second photon performs the second transition between the excited state and the conduction band, thus performing a photo-ionization of the center.



Electrons released from  $\text{F}_2^{2+}(\text{2Mg})$ -centers as a result of the photo-ionization process are captured by deep traps and other nearby  $\text{F}_2^{2+}(\text{2Mg})$ - and  $\text{F}^+$ -centers:



The above-described deep trapping sites are able to store information almost indefinitely. The result of these photochromic transformations is (a) a creation of another charged state of the aggregate defect,  $\text{F}_2^+(\text{2Mg})$ -center, having three localized electrons and characterized by the absorption bands at 260, 335, and 620 nm, or (b) a creation of a neutral F-center with a UV absorption band at 205 nm.

Two types of fluorescent processes for “reading” data were suggested and tested. The Type 1, or “negative” process, involves stimulation of original green fluorescence of  $\text{F}_2^{2+}(\text{2Mg})$ -centers using blue laser light excitation at  $435 \pm 40$  nm. The intensity of this excitation was significantly reduced to avoid two-photon absorption, but it was sufficient to generate green fluorescence strong enough for the reliable detection of information. Small volumes of  $\text{Al}_2\text{O}_3$  crystal (bits) subjected to two-photon absorption/ionization during “writing” show reduced intensity of fluorescence whereas the “unwritten” bits show high intensity of green fluorescence. The type 2 readout process, or so-called “positive” readout process, involves using laser excitation at  $335 \pm 30$  nm or  $620 \pm 50$  nm to stimulate the 750 nm fluorescence of  $\text{F}_2^+(\text{2Mg})$ -centers created during “writing.”

## CONCLUSIONS

Spectroscopic properties of the new  $\text{Al}_2\text{O}_3:\text{C,Mg}$  crystals were studied. Several types of Mg-impurity associated aggregate oxygen vacancy defects were investigated in comparison with double vacancy defects identified in neutron and proton irradiated sapphire crystals [5,6]. New color centers have a strong anisotropy of opti-



cal absorption and fluorescence. Quantum yield of fluorescence was measured in comparison with standard dyes and found to be very high. Electronic processes and photochromic transformations were discussed in assumption of sequential two-photon absorption followed by ionization and trapping of electrons. The mechanism of “writing” and “reading” information using laser light is described. Nondestructive “reading” utilizing one-photon absorption is used. The new  $\text{Al}_2\text{O}_3:\text{C},\text{Mg}$  crystals are suggested as a promising medium for high capacity bit-wise volumetric optical data storage that allows one to use compact CW blue laser diodes.

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