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(PO Box MG-54, Magurele RO-77125, Romania)**CUBIC OPTICAL NONLINEARITY  
OF THIN Fe<sub>2</sub>O<sub>3</sub> AND Cr<sub>2</sub>O<sub>3</sub> FILMS SYNTHESIZED  
BY PULSED LASER DEPOSITION**PACS 42.70.Mp, 78.20.-e,  
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The extinction spectra and the parameters of cubic optical nonlinearity in thin Fe<sub>2</sub>O<sub>3</sub> and Cr<sub>2</sub>O<sub>3</sub> films deposited on glass substrates with the use of the laser sputtering method have been measured. The cubic optical nonlinearity is studied, by using femtosecond laser radiation with the wavelength  $\lambda = 800$  nm and the pulse duration  $\tau = 180$  fs. The energy gap width evaluated from the extinction spectra is found to equal  $E_g \approx 2.4$  eV and 2.2 eV for Fe<sub>2</sub>O<sub>3</sub> films synthesized on the substrates at temperatures of 293 K and 800 K, respectively, and  $E_g \approx 3$  eV for Cr<sub>2</sub>O<sub>3</sub> films deposited on the substrate heated up to 800 K. Rather high values are obtained for the coefficients of refractive nonlinearity:  $Re\chi^{(3)} \sim 10^{-6}$  esu for Fe<sub>2</sub>O<sub>3</sub> films and  $Re\chi^{(3)} \sim 10^{-7}$  esu for Cr<sub>2</sub>O<sub>3</sub> ones. The determined values of  $Im\chi^{(3)}$  amounted to about  $10^{-6} \div 10^{-7}$  esu for Fe<sub>2</sub>O<sub>3</sub> films and about  $10^{-8}$  esu for Cr<sub>2</sub>O<sub>3</sub> ones. Probable mechanisms of refractive nonlinearity have been proposed.

*Key words:* cubic optical nonlinearity, thin Fe<sub>2</sub>O<sub>3</sub> and Cr<sub>2</sub>O<sub>3</sub> films, laser sputtering method, femtosecond laser radiation.

**1. Introduction**

The search for nonlinear optical media with a high cubic nonlinearity and a high operation rate of this nonlinearity remains an important problem for needs of modern optoelectronics. Recently, it has been demonstrated in a number of works [1–6] that low-dimensional structures (thin films, nanoparticle composites) of transition metal oxides, in particular, Fe<sub>2</sub>O<sub>3</sub>, are characterized by rather a high refractive nonlinearity and represent a considerable practical interest. For instance, in work [1], the coefficient of cubic nonlinear susceptibility  $\chi^{(3)} = 2 \times 10^{-9}$  esu was obtained at the laser wavelength  $\lambda = 480$  nm and the laser pulse duration  $\tau = 180$  fs for amorphous Fe<sub>2</sub>O<sub>3</sub> films fabricated, by using the sol-gel method. For crystalline  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> and  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> films synthesized within the same method, the  $\chi^{(3)}$ -values obtained under the nanosec-

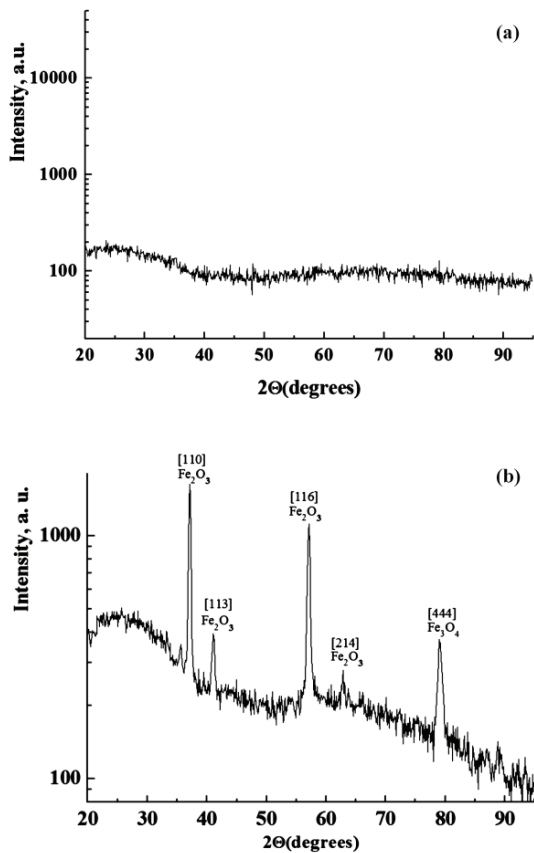
ond laser radiation with  $\lambda = 1.9$   $\mu$ m and  $\tau = 10$  ns were  $5.8 \times 10^{-11}$  esu and  $2.1 \times 10^{-11}$  esu, respectively [3]. In work [6], the value  $\chi^{(3)} = 5 \times 10^{-6}$  esu was obtained for Fe<sub>2</sub>O<sub>3</sub> films fabricated using the laser ablation method and picosecond laser radiation ( $\lambda = 532$  nm,  $\tau = 30$  ps).

The available data testify that the magnitude of cubic nonlinearity in Fe<sub>2</sub>O<sub>3</sub> films depends substantially on the film manufacturing methods, film structure, and parameters of laser radiation used at measurements. Therefore, it seems important to obtain data concerning the nonlinear optical response of Fe<sub>2</sub>O<sub>3</sub> films grown up with the use of the pulsed laser sputtering method, when laser pulses of femtosecond duration are applied.

Fe<sub>2</sub>O<sub>3</sub> is a semiconductor with the energy gap width  $E_g = 2.2$  eV [7]. It is transparent in the visible spectral range. With the aim in view to find a nonlinear optical material with a wider transparency window, we also considered chromium oxide (Cr<sub>2</sub>O<sub>3</sub>) with the energy gap width  $E_g = 3.4$  eV [8]. This is

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**Fig. 1.** XRD patterns of nano-scale  $\text{Fe}_2\text{O}_{3-x}$  films deposited, by using the reactive laser deposition method on  $\text{SiO}_2$  substrates: at  $T_s = 293$  K and  $P_{\text{O}_2} = 0.1$  Pa, (a) and at  $T_s = 800$  K and  $P_{\text{O}_2} = 0.1$  Pa (b)

a material that is promising for the creation of selective absorbing films for the solar energy conversion and so on [9]. In earlier works, linear optical and spectral properties of thin  $\text{Cr}_2\text{O}_3$  films fabricated by, in particular, the chemical vapor deposition [10] and chemical pyrolysis sputtering [11] techniques showed that the spectrum shape depends to some extent on the method of film fabrication. However, the nonlinear optical properties of  $\text{Cr}_2\text{O}_3$  films, unlike those of  $\text{Fe}_2\text{O}_3$  ones, have not been studied enough. In particular, we did not manage to find works dealing with the cubic optical nonlinearity in  $\text{Cr}_2\text{O}_3$  films, although the theoretical [12] and experimental [13] researches of the quadratic nonlinearity (the second harmonic generation) are known.

In this work, with the help of femtosecond laser radiation ( $\lambda = 800$  nm,  $\tau = 180$  fs), the coefficient of

cubic susceptibility  $\chi^{(3)}$  was measured in amorphous and crystalline  $\text{Fe}_2\text{O}_3$  and  $\text{Cr}_2\text{O}_3$  films synthesized by the pulsed laser sputtering at various substrate temperatures and various oxygen pressures in a vacuum chamber. Possible mechanisms of cubic nonlinearity in the examined films are analyzed.

## 2. Experimental Part

### 2.1. Sample fabrication

Nano-sized films of iron and chromium oxides were synthesized using the method of reactive pulsed laser deposition onto  $\text{SiO}_2$  substrates. The deposition was carried out in a vacuum reactor made of stainless steel. In order to avoid the contamination, the vacuum chamber was pumped out to a residual pressure of about  $4.5 \times 10^{-5}$  Pa before every deposition. Pure oxygen (99.999%) was let into the chamber until its dynamic pressure became stabilized at values of 0.1, 0.5, or 1.0 Pa. Pure Fe (99.5%) was knocked out from a target with the help of radiation emitted by a KrF ( $\lambda = 248$  nm) pulsed excimer laser with an energy density of  $4.0$  J/cm<sup>2</sup>, a pulse repetition frequency of 10 Hz, and a pulse duration of about 25 ns. Every film was deposited by applying a definite number of laser pulses (4000, 5000, and 6000, respectively) corresponding to the oxygen pressure in the reactor. In order to avoid the breakdown and to provide the ablation process smoothness, the target was rotated at a rotation frequency of 3 Hz. Before each deposition, the target surface was cleaned, making use of 3000 laser pulses, provided that the substrate was closed.

The flux of knocked out iron ions was gathered on the  $\text{SiO}_2$  substrate, which had been cleaned in an ultrasonic bath with ethanol and deionized by water. The substrate was arranged in parallel to the target and at a distance of 45 mm from the latter. The thickness of deposited films was measured with the help of a profilometer "Tensor Instruments", the model "Alpha-step 100", with an error of 5%. The X-ray diffraction (XRD) analysis of  $\text{Fe}_2\text{O}_3$  films was carried out with the help of an X-ray diffractometer "Stoe" at 45 kW and 33 mA ( $\text{Cu } K_\alpha$  radiation). The corresponding results showed that the films deposited on the  $\text{SiO}_2$  substrate at room temperature ( $T_s = 293$  K) had an amorphous structure, whereas the films deposited on the same substrate but heated up to the temperature  $T_s = 800$  K had a polycrystalline structure. This can be seen in Fig. 1, where the XRD patterns for those two film types are exhibited.

The results of our researches showed that the films, which were obtained at a higher oxygen pressure, contained a larger amount of oxidized iron or chromium than the samples deposited at a lower pressure. Moreover, the higher the oxygen pressure, the thinner was the film deposited on the  $\text{SiO}_2$  substrate, by using the same number of laser pulses.

It should be noted that polycrystalline films, besides the main  $\text{Fe}_2\text{O}_3$  phase, also included a small amount of  $\text{Fe}_3\text{O}_4$  phase with the energy gap width  $E_g = 0.1$  eV [14]. Unfortunately, the X-ray diffraction analysis of  $\text{Cr}_2\text{O}_3$  films was not done.

## 2.2. Experimental technique of optical researches

Extinction spectra in the interval from 300 to 1100 nm were measured with the help of a monochromator MDR-6. The absorption coefficient of the sample was calculated using the formula

$$\alpha = \frac{1}{L} \ln \frac{(1-R)^2}{T}, \quad (1)$$

where  $T$  is the sample transmittance,  $L$  the sample thickness, and  $R$  the reflectance from the sample surface, which was evaluated on the basis of the refractive index:  $n_0 = 2.75$  for  $\text{Fe}_2\text{O}_3$  and  $n_0 = 2.5$  for  $\text{Cr}_2\text{O}_3$  [15].

The research of optical nonlinearity was carried out with the help of the known  $Z$ -scan technique [16]. The scheme of experimental installation is shown in Fig. 2. In our experiment, we used a titanium-doped sapphire laser with the generation wavelength  $\lambda = 800$  nm, a pulse repetition frequency of 75 MHz, and the pulse duration  $\tau = 180$  fs. The laser beam was focused by a lens with a focal length of 35 cm. The beam waist diameter in various cases amounted to 36 or 29  $\mu\text{m}$ . The laser beam intensity at the focus,  $I_0$ , was 0.3 and 0.9  $\text{GW}/\text{cm}^2$ , respectively, and the aperture transmittance  $S$  was equal to 0.169 and 0.121, respectively.

The coefficient of refractive index nonlinearity,  $n_2$ , and the real part of cubic nonlinear susceptibility,  $\text{Re}\chi^{(3)}$ , were calculated, by using the data obtained for the normalized transmittance in the scheme of  $Z$ -scan experiment with the closed aperture (CA), by the well-known expressions [16, 17]

$$n_2 = \frac{\Delta T_{p-v} \lambda}{0.406(1-S)^{0.27} 2\pi I_0 L_{\text{eff}}}, \quad (2)$$

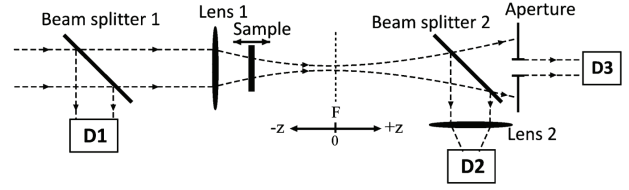


Fig. 2. Schematic diagram of the experimental installation for measuring the parameters of cubic nonlinearity

$$\text{Re}\chi^{(3)} (\text{esu}) = \frac{3n_0^2 n_2}{160\pi^2} (\text{m}^2\text{W}^{-1}), \quad (3)$$

where  $\Delta T_{p-v}$  is the normalized difference between the transmittance maximum and minimum in the CA scheme,  $S$  the aperture transmittance (the fraction of radiation that reached a photodiode),  $I_0$  the light intensity at the focus point,  $n_0$  the linear refractive index, and  $L_{\text{eff}} = [1 - \exp(-\alpha L)]/\alpha$  is the effective length of the sample.

In the case of the scheme with the open aperture (OA), the coefficient of nonlinear absorption  $\beta$  was calculated on the basis of the following approximation for the obtained normalized transmittance data [14]:

$$T(z) = -\frac{q_0}{2\sqrt{2}} \frac{1}{[1 + z^2/z_0^2]} \quad \text{at} \quad |q_0| \ll 1, \quad (4)$$

where  $q_0(z) = \beta I_0 L_{\text{eff}}$ .

The imaginary part of the coefficient of third-order nonlinear susceptibility,  $\text{Im}\chi^{(3)}$ , is related to the coefficient of nonlinear absorption  $\beta$  by the relation [16]

$$\text{Im}\chi^{(3)} (\text{esu}) = \frac{c^2 n_0^2 \beta}{240\pi^2 \omega} (\text{mW}^{-1}), \quad (5)$$

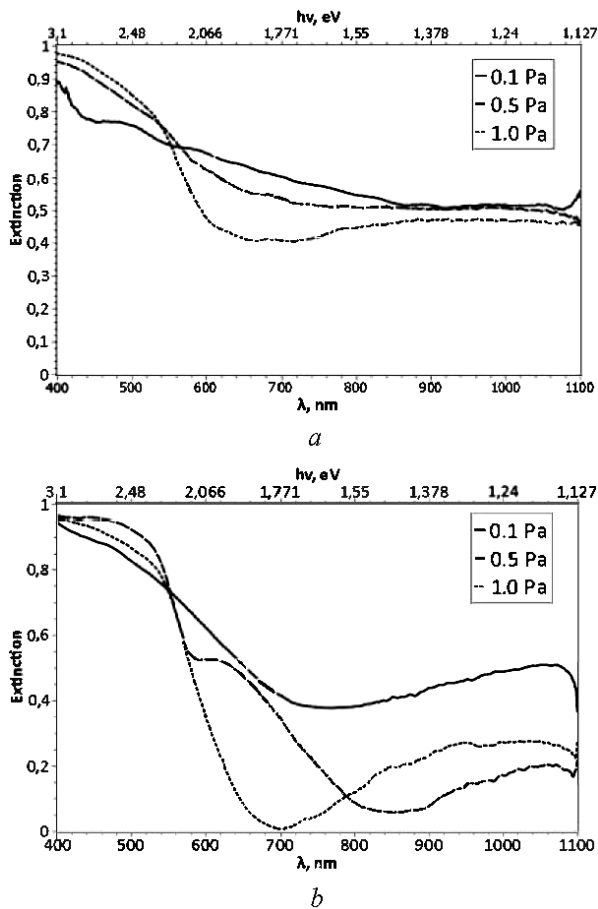
where  $\omega$  is the light field frequency.

## 3. Results and Their Discussion

### 3.1. Extinction spectra

The extinction spectra of the examined  $\text{Fe}_2\text{O}_3$  films synthesized at various oxygen pressures in the chamber (0.1, 0.5, and 1 Pa) are depicted in Fig. 3. Panel *a* corresponds to amorphous films obtained on the substrate with the temperature  $T_s = 293$  K, and panel *b* to polycrystalline films obtained on the substrate heated to the temperature  $T_s = 800$  K.

From Fig. 3, *a*, one can see that the shape of extinction curves for the studied films changes rather substantially from sample to sample. The extinction curve of the amorphous film obtained at an oxygen



**Fig. 3.** Extinction spectra of amorphous  $\text{Fe}_2\text{O}_3$  films (a) and polycrystalline  $\text{Fe}_2\text{O}_3$  films (b) synthesized at various oxygen pressures in a reactor

pressure of 0.1 Pa demonstrates a smooth recession of absorption from shorter to longer wavelengths with no distinctly pronounced edge. In the curve corresponding to the amorphous film obtained at an oxygen pressure of 0.5 Pa, one can see a shoulder in the wavelength interval of 520–680 nm. For the film obtained at an oxygen pressure of 1 Pa, this shoulder becomes rather sharp and located in the interval of 520–600 nm. This shoulder testifies to the presence of quasiforbidden gap in the films concerned. Being estimated by the shoulder shape, the width of this gap,  $E'_g$ , was found to equal approximately 2.4 eV, which is close to the energy gap width in  $\alpha\text{-Fe}_2\text{O}_3$  [7].

Hence, the amorphous films can be considered as semiconductors with characteristic tails of the density of states near the edges of the valence and con-

duction bands, and with a set of various local levels in the quasiforbidden gap. The shape of extinction curves confirms this conclusion. In the interval of 900–1000 nm, an extinction plateau is observed at approximately the same, rather high, level for all three films.

The extinction curves for polycrystalline films (Fig. 3, b) changed their shape considerably. The absorption edge became sharper, especially for the film grown at the maximum oxygen pressure of 1 Pa. Moreover, it is a little shifted toward long waves in comparison with the amorphous sample spectrum. Attention is attracted by the appearance of rather a pronounced “hump” at  $\lambda \approx 630$  nm in the spectrum of the film obtained at an oxygen pressure of 0.5 Pa, and the presence of deep and wide valleys in the spectra of the films synthesized at oxygen pressures of 0.5 ( $\lambda \approx 700$  nm) and 1 Pa ( $\lambda \approx 830$  nm).

As was marked above (see Fig. 1, b), the polycrystalline  $\text{Fe}_2\text{O}_3$  films fabricated at the oxygen pressure in a chamber  $P_{\text{O}_2} = 0.1$  Pa contained the crystalline phase  $\text{Fe}_3\text{O}_4$ . This fact explains the higher absorption and the spectrum structure in the interval of 700–1100 nm (the intrinsic absorption range for  $\text{Fe}_3\text{O}_4$ ) for this specimen and is confirmed by the absorption spectra of  $\text{Fe}_3\text{O}_4$  films measured in work [3].

We also studied  $\text{Cr}_2\text{O}_3$  films deposited on glass substrates. One of them was deposited at a temperature of 293 K and a pressure of 0.5 Pa in a chamber. Two others were deposited on substrates heated up to a temperature of 800 K and at an oxygen pressure of 0.1 or 0.5 Pa in a chamber. By analogy with  $\text{Fe}_2\text{O}_3$ , we may assume that the film deposited at a substrate temperature of 293 K is amorphous, and those deposited at a substrate temperature of 800 K are polycrystalline. The extinction curves measured for those films in the interval of 380–1100 nm are shown in Fig. 4.

From Fig. 4, one can see that the spectra of all three films had a more or less sloping edge in the interval of 400–450 nm. The edge is the sharpest for the film deposited at a substrate temperature of 800 K and the oxygen pressure  $P_{\text{O}_2} = 0.1$  Pa. The films deposited at  $P_{\text{O}_2} = 0.5$  Pa had more extended edges. The value of  $E_g$  determined from the shape of absorption edge for the film deposited at an oxygen pressure of 0.1 Pa in the sputtering chamber was found to equal 3 eV. In the spectral interval of 500–1100 nm, there is a considerable damping background

with appreciable maxima at 600 and 940 nm, which are most likely associated with extrinsic absorption.

### 3.2. Nonlinear optical properties

#### 3.2.1. $\text{Fe}_2\text{O}_3$

Nonlinear optical parameters were measured for two groups of  $\text{Fe}_2\text{O}_3$  thin film samples. One of them included the films deposited on the substrate at a temperature of 293 K and oxygen pressures of 0.1, 0.5, and 1 Pa in a chamber. The other group included the films deposited on the substrate heated to a temperature of 800 K and at the same oxygen pressures in a chamber. As was mentioned above, the films in the former group had an amorphous structure, and those in the latter group a polycrystalline one. In Fig. 5, the dependences of the normalized transmittance of the  $\text{Fe}_2\text{O}_3$  film deposited at  $T_s = 293$  K and  $P_{\text{O}_2} = 1$  Pa on its  $Z$ -position with respect to the focus (the  $Z$ -scan scheme) are exhibited. These dependences were used to determine the parameters of cubic nonlinearity:  $\text{Re}\chi^{(3)}$ ,  $\text{Im}\chi^{(3)}$ ,  $n_2$ , and  $\beta$ . The corresponding values obtained for the analyzed  $\text{Fe}_2\text{O}_3$  films are listed in Table 1. In the table,  $T_s$  is the substrate temperature,  $P_{\text{O}_2}$  the oxygen pressure in the chamber,  $L$  the sample thickness, and  $I_0$  the light intensity at the lens focus.

From Table 1, one can see that, for the amorphous films that were fabricated at oxygen pressures of 0.5 and 1 Pa, the values of  $\text{Re}\chi^{(3)}$  turned out by an order of magnitude larger than their counterparts for the polycrystalline films. The values of  $\text{Re}\chi^{(3)}$  are positive for all samples. The maximum value of the real part of cubic nonlinear susceptibility,  $\text{Re}\chi^{(3)} = 6.45 \times 10^{-6}$  esu, was obtained for the amorphous film deposited at an oxygen pressure of 0.5 Pa in a chamber.

Table 1 also contains the coefficients of nonlinear absorption  $\beta$ . The lowest  $\beta$ -value was obtained for the amorphous film synthesized at an oxygen pressure of 0.5 Pa. The  $\text{Re}\chi^{(3)}$ -value for this sample turned out the largest.

We would like to make the following remark concerning the probable origin of refractive nonlinearity. It is known [18] that the positive refractive nonlinearity in semiconductors can be connected with the nonlinear polarization of bound electrons (the Kerr nonlinearity) or with the processes of intraband scattering of equilibrium electrons under the influence of

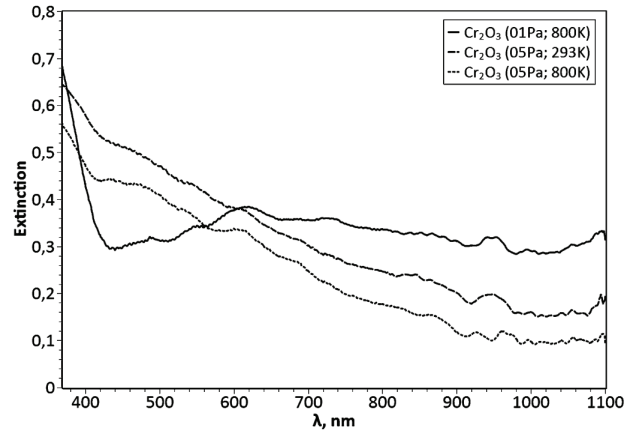


Fig. 4. Extinction spectra of amorphous and polycrystalline  $\text{Cr}_2\text{O}_3$  films synthesized at various oxygen pressures in the reactor

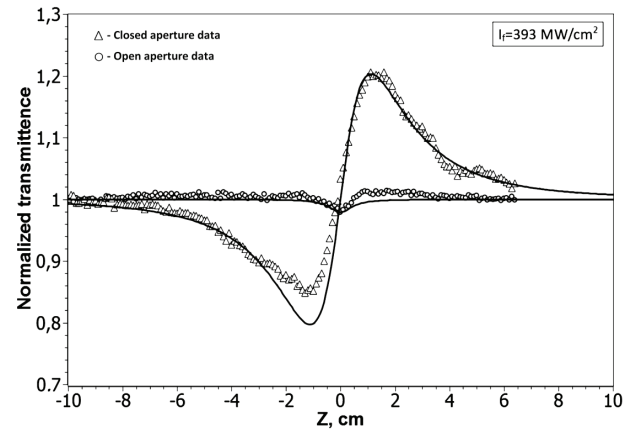


Fig. 5.  $Z$ -scan dependences of the normalized transmittance of the  $\text{Fe}_2\text{O}_3$  film deposited at  $T_s = 293$  K and an oxygen pressure of 1 Pa on the film position  $Z$  with respect to the focus in the femtosecond experiment ( $\lambda = 800$  nm). The solid curve demonstrates the corresponding theoretical approximation

intensive light radiation. With regard for the shape of extinction curves, namely, rather a high absorption background and the smeared edge of intrinsic absorption, it is possible to assume the presence of various impurity levels in the energy gap, in particular, near the conduction band bottom, and, hence, the presence of a considerable concentration of equilibrium electrons thermally excited at room temperature, at which the nonlinear optical measurements were carried out. Rather a high dark conductivity of the film also testifies to this assumption. Therefore, it is highly probable that the refractive nonlinearity of

Table 1. Nonlinear optical parameters of examined Fe<sub>2</sub>O<sub>3</sub> films

Sample	$T_s$ , K	$P_{O_2}$ , Pa	$L$ , $\mu\text{m}$	$\alpha$ , $\text{cm}^{-1}$	$I_0$ , $\text{GW}/\text{cm}^2$	$n_2$ , $\text{cm}^2/\text{W}$	$\beta$ , $\text{cm}/\text{W}$	$\text{Re}\chi^{(3)}$ , esu	$\text{Im}\chi^{(3)}$ , esu
Fe <sub>2</sub> O <sub>3</sub>	293	0.1	0.053	$1.826 \times 10^5$	0.393	$4.541 \times 10^{-9}$	$2.433 \times 10^{-5}$	$6.524 \times 10^{-7}$	$2.965 \times 10^{-8}$
Fe <sub>2</sub> O <sub>3</sub>	293	0.5	0.026	$3.429 \times 10^5$	0.393	$4.491 \times 10^{-8}$	$1.433 \times 10^{-4}$	$6.453 \times 10^{-6}$	$1.747 \times 10^{-7}$
Fe <sub>2</sub> O <sub>3</sub>	293	1.0	0.013	$5.808 \times 10^5$	0.393	$3.288 \times 10^{-8}$	$1.671 \times 10^{-4}$	$4.724 \times 10^{-6}$	$2.037 \times 10^{-7}$
Fe <sub>2</sub> O <sub>3</sub>	800	0.1	0.06	$1.09 \times 10^5$	0.866	$5.826 \times 10^{-9}$	$2.623 \times 10^{-5}$	$8.37 \times 10^{-7}$	$3.197 \times 10^{-8}$
Fe <sub>2</sub> O <sub>3</sub>	800	0.5	0.045	$0.441 \times 10^5$	0.866	$3.97 \times 10^{-9}$	$2.434 \times 10^{-4}$	$5.704 \times 10^{-7}$	$2.967 \times 10^{-7}$
Fe <sub>2</sub> O <sub>3</sub>	800	1.0	0.04	$1.001 \times 10^5$	0.351	$3.195 \times 10^{-8}$	$3.461 \times 10^{-5}$	$4.59 \times 10^{-7}$	$4.218 \times 10^{-8}$

Table 2. Nonlinear optical parameters of examined Cr<sub>2</sub>O<sub>3</sub> films

Sample	$T_s$ , K	$P_{O_2}$ , Pa	$L$ , $\mu\text{m}$	$\alpha$ , $\text{cm}^{-1}$	$I_0$ , $\text{GW}/\text{cm}^2$	$n_2$ , $\text{cm}^2/\text{W}$	$\beta$ , $\text{cm}/\text{W}$	$\text{Re}\chi^{(3)}$ , esu	$\text{Im}\chi^{(3)}$ , esu
Cr <sub>2</sub> O <sub>3</sub>	800	0.1	0.07	$7.232 \times 10^4$	0.866	$6.283 \times 10^{-10}$	$7.993 \times 10^{-6}$	$7.46 \times 10^{-8}$	$8.05 \times 10^{-9}$
Cr <sub>2</sub> O <sub>3</sub>	293	0.5	0.055	$8.595 \times 10^4$	0.866	$1.472 \times 10^{-9}$	$-1.371 \times 10^{-5}$	$1.748 \times 10^{-7}$	$-1.381 \times 10^{-8}$
Cr <sub>2</sub> O <sub>3</sub>	800	0.5	0.07	$5.891 \times 10^4$	0.866	$1.04 \times 10^{-9}$	$2.578 \times 10^{-5}$	$1.235 \times 10^{-7}$	$2.597 \times 10^{-8}$

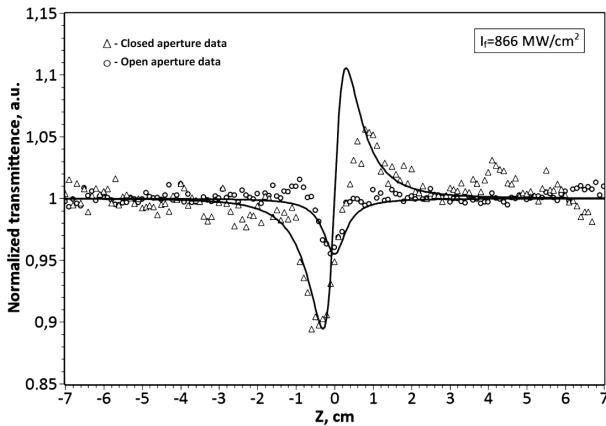


Fig. 6. The same as in Fig. 5, but for the Cr<sub>2</sub>O<sub>3</sub> film deposited at  $T_s = 800$  K and an oxygen pressure of 0.5 Pa

researched films is associated, to a great extent, with the processes of intraband scattering of equilibrium charge carriers, if the non-parabolic character of the conduction band is taken into account and owing to the dependence of the relaxation time of electrons in the band on their energy. In this case, the “Kerr” nonlinearity may also make a contribution to the value of  $\text{Re}\chi^{(3)}$ .

### 3.2.2. Cr<sub>2</sub>O<sub>3</sub>

In Fig. 6, the dependence of the normalized transmittance of a Cr<sub>2</sub>O<sub>3</sub> film on the  $Z$ -position of the film with respect to the focus in the  $Z$ -scan scheme measured at the substrate temperature  $T_s = 800$  K and

an oxygen pressure of 0.5 Pa is shown. Table 2 contains the corresponding values of nonlinear optical parameters for the examined Cr<sub>2</sub>O<sub>3</sub> films at  $\lambda = 800$  nm determined from the  $Z$ -scan curves. The notations are the same as in Table 1.

One can see that the refractive nonlinearity  $\text{Re}\chi^{(3)}$  is positive for all samples, i.e. self-focusing takes place. The maximum value  $\text{Re}\chi^{(3)} = 1.75 \times 10^{-7}$  esu was obtained for the amorphous film deposited at an oxygen pressure of 0.5 Pa. The values of  $\text{Re}\chi^{(3)}$  for the polycrystalline films deposited at oxygen pressures of 0.1 and 0.5 Pa were of the same order, but 2.2 and 1.4, respectively, times lower than the maximum. By comparing those values with the data obtained for the Fe<sub>2</sub>O<sub>3</sub> films, we see that they are approximately an order of magnitude smaller.

Analogously to the case of Fe<sub>2</sub>O<sub>3</sub> films, the refractive nonlinearity in the Cr<sub>2</sub>O<sub>3</sub> ones can be connected with the cumulative contribution made by the processes of intraband scattering of free equilibrium electrons and nonlinear polarization of bound electrons. Taking into account that the wavelength of an applied laser was 800 nm, the shift from the absorption edge is much larger in the Cr<sub>2</sub>O<sub>3</sub> case. Therefore, the contribution of the nonlinear polarization of bound electrons in Cr<sub>2</sub>O<sub>3</sub> can be smaller than in Fe<sub>2</sub>O<sub>3</sub>.

## 4. Conclusions

With the help of the  $Z$ -scan method and making use of laser radiation ( $\lambda = 800$  nm,  $\tau = 180$  fs), the

parameters of cubic optical nonlinearity were measured in thin (nano-sized) Fe<sub>2</sub>O<sub>3</sub> and Cr<sub>2</sub>O<sub>3</sub> films deposited on glass substrates using the laser ablation technique. Depending on the substrate temperature at the sputtering,  $T_s$ , the Fe<sub>2</sub>O<sub>3</sub> and Cr<sub>2</sub>O<sub>3</sub> films had either an amorphous ( $T_s = 293$  K) or polycrystalline ( $T_s = 800$  K) structure. The energy gap width  $E_g$  evaluated from the extinction spectra was found to equal  $E_g \approx 2.4$  eV and  $E_g \approx 2.2$  eV for Fe<sub>2</sub>O<sub>3</sub> films synthesized on the substrates at temperatures 293 and 800 K, respectively, and  $E_g \approx 3$  eV for Cr<sub>2</sub>O<sub>3</sub> films deposited on the substrate heated to 800 K. The coefficient of cubic nonlinear susceptibility  $\text{Re}\chi^{(3)}$  was determined to be of an order of  $10^{-6}$  or  $10^{-7}$  esu for Fe<sub>2</sub>O<sub>3</sub> films with the amorphous or polycrystalline structure, respectively. The largest value  $\text{Re}\chi^{(3)} = 6.45 \times 10^{-6}$  esu was obtained for the amorphous Fe<sub>2</sub>O<sub>3</sub> film deposited at an oxygen pressure of 0.5 Pa in the sputtering chamber. All iron oxide films revealed a nonlinear absorption with the coefficient  $\beta$  of about  $10^{-4}$ – $10^{-5}$  cm/W. At the same time, the Cr<sub>2</sub>O<sub>3</sub> films obtained at  $T_s = 800$  K showed a nonlinear absorption with  $\beta \sim 10^{-5}$  cm/W, whereas the Cr<sub>2</sub>O<sub>3</sub> films sputtered at  $T_s = 293$  K demonstrated a nonlinear enlightenment. The most probable mechanisms of refractive nonlinearities in all studied specimens seem to be the “Kerr” nonlinearity and the intraband scattering of equilibrium electrons under the influence of laser radiation. Rather high values of refractive non-linearity in the examined film materials make them promising for practical applications in optoelectronic devices.

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ОПТИЧНА КУБІЧНА  
НЕЛІНІЙНІСТЬ ТОНКИХ ПЛІВОК  
Fe<sub>2</sub>O<sub>3</sub> І Cr<sub>2</sub>O<sub>3</sub>, СИНТЕЗОВАНИХ МЕТОДОМ  
ІМПУЛЬСНОГО ЛАЗЕРНОГО ОСАДЖЕННЯ

Резюме

Проведено вимірювання спектрів екстинкції та параметрів оптичної кубічної нелінійності тонких плівок Fe<sub>2</sub>O<sub>3</sub> та Cr<sub>2</sub>O<sub>3</sub>, осаджених на скляні підкладки методом імпульсного лазерного напилення. Дослідження оптичної кубічної нелінійності проводилось з використанням фемтосекундного випромінювання на довжині хвилі  $\lambda = 800$  нм з тривалістю імпульсів  $\tau = 180$  фс. Оцінені за спектрами екстинкції ширини заборонених зон дорівнюють, відповідно,  $E_g \sim 2,4$  eV і 2,2 eV для плівок Fe<sub>2</sub>O<sub>3</sub>, синтезованих на підкладку при температурах 293 К і 800 К та  $E_g \sim 3$  eV для плівок Cr<sub>2</sub>O<sub>3</sub>, осаджених на підкладку, нагріту до 800 К. Отримано достатньо високі значення коефіцієнтів рефрактивної нелінійності  $\text{Re}\chi^{(3)} \sim 10^{-6}$  esu для плівок Fe<sub>2</sub>O<sub>3</sub> і  $\text{Re}\chi^{(3)} \sim 10^{-7}$  esu для плівок Cr<sub>2</sub>O<sub>3</sub>. Визначені величини  $\text{Im}\chi^{(3)}$  становили по порядку для Fe<sub>2</sub>O<sub>3</sub> –  $10^{-6}$ – $10^{-7}$  esu, а для плівок Cr<sub>2</sub>O<sub>3</sub> –  $10^{-8}$  esu. Запропоновані можливі механізми рефрактивної нелінійності.