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Optical and nonlinear optical characterization of nanostructured oxyhydroxide of aluminium

V.Ya.Gayvoronsky, M.A.Kopylovsky, E.A.Vishnyakov, A.N.Khodan[*], *J.-L.Vignes*[**], *M.N.Esaulkov*[***], *A.P.Shkurinov*[***]

Institute of Physics, National Academy of Sciences of Ukraine,
46 pr. Nauky, 03680 Kyiv, Ukraine
[*]A.Frumkin Institute of Physical Chemistry and Electrochemistry,
Russian Academy of Sciences, 31 Leninsky pr., 119991 Moscow, Russia
[**]LIMHP, University Paris-Nord, 99, av. J.B.Clement,
93430 Villetaneuse, France
[***]Department of Physics and International Laser Center,
M.Lomonosov Moscow State University, 119892 Moscow, Russia

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The diffusion transmittance spectra, scattering indicatrix and nonlinear optical (NLO) response within picosecond range laser pulses excitation were studied for a novel functional material — ultraporous nanostructured oxyhydroxide of aluminium (NOA). The contribution of two mechanisms of photoinduced extinction enhancement was observed at the fundamental wavelength 1064 nm of Nd:YAG laser that is similar to the NLO response of porous layers of titanium dioxide and silicon layers. The nonmonotonic behavior with photobleaching effect due to the resonance excitation of the NOA surface states was measured at the laser second harmonic wavelength. This effect can be utilized for the optical control of the states of molecules adsorbed at the NOA surface in spectroscopy and for random lasing applications.

Проведено исследование спектров диффузного пропускания, индикатрисы рассеяния и нелинейно-оптического (НЛО) отклика при возбуждении лазерными импульсами пикосекундного диапазона нового функционального материала — ультрапористого наноструктурированного оксигидрооксида алюминия (НОА). Наблюдался вклад двух механизмов фотоиндуцированного увеличения экстинкции на фундаментальной длине волны излучения 1064 нм Nd:АИГ лазера, который подобен НЛО отклику пористых слоев диоксида титана и кремния. На длине волны второй гармоники лазера наблюдался немонотонный характер НЛО отклика с типичным проявлением эффекта увеличения пропускания вследствие резонансного возбуждения поверхностных состояний НОА. Обнаруженные эффекты могут быть использованы для управления оптическими методами состоянием адсорбированных на поверхности НОА молекул для спектроскопических приложений и для получения случайной лазерной генерации в сильно рассеивающей среде.

Using of transparent matrix partially filled with different oxides, semiconductors or organic dyes is a simple and very capable way for designing of novel guest-host functional materials and composites. The ultraporous nanostructured oxyhydroxides of aluminium (NOA) is a medium possessing high specific surface suitable for molecular adsorption and nanoparticles deposition. Incorporation of various guest systems into the NOA matrix allows basic research of the interaction with adsorbates or even an enhancement of guest subsystem response by the local field of the matrix. For applied

reasons it is interesting to study spectroscopic properties of such functional composites in the UV-visible-IR-THz domain, to create novel random lasing media, to provide photoinduced control of the THz range response by carriers dynamics manipulation etc.

Synthesis of the NOA is based on selective oxidation of the surface of liquid alloys in a humid atmosphere at elevated temperature. Two synthesis methods based on the Hg alloys and the Ga alloys are using now [1, 2]. Both methods provides similar properties of NOA: density 0.02–0.04 g/cm^3, high porosity >99 vol. % and large specific surface — up to 800 m^2/g. The NOA structure consists of amorphous nanofibrils with typical length 120–150 nm and diameter ~5 nm, having the composition $Al_2O_3 \cdot nH_2O$, n = 3.0–3.6 [1, 2]. The photo of the grown native NOA monolith and a TEM image of the fibrous structure of NOA are presented at Fig. 1a and b correspondingly. The image was obtained at the temperature ~80 K in order to suppress the water loss and decomposition of the sample (water content up to 30 wt. %).

For the optical measurements we used samples with typical number of water molecules n ~ 3.5–3.6 pressed into pellets with diameter about 13 mm, and typical thickness 0.25 mm. The pressed samples density was 0.131 g/cm^3 that corresponds to porosity (voids volume fraction) ~95 % and specific surface area 260–300 m2/g.

From the optical point of view the NOA pelletre presents typical scattering object in the visible range. Its optical response is very sensitive to the sample point and aperture of the probing beam. Typical spectral dependencies of the optical density of the sample for different points are presented at Fig. 2a. The sample was illuminated with wide aperture beam; the 5 mm diaphragm was positioned just behind the sample. The short focus 3 cm lens focused image of the diaphragm at the edge of the fiber coupled with CCD spectrometer. The curves were obtained for the different position of the diaphragm across the pellet and demonstrate an optical inhomogeneity of the sample with common features: (i) extinction enhancement in the range 440–495 nm, (ii) nonmonotonic response 495–550 nm consisting of two peaks with decrease of the extinction at 510 and 533 nm, (iii) almost flat Mie-type response in the 550–900 nm range, (iv) transmittance enhancement at wavelength longer than 900 nm. Preliminary FTIR measurements with thinner plates have shown the transmittance growth till 2 μm that changes to the sample darkening at 2.7 μm.

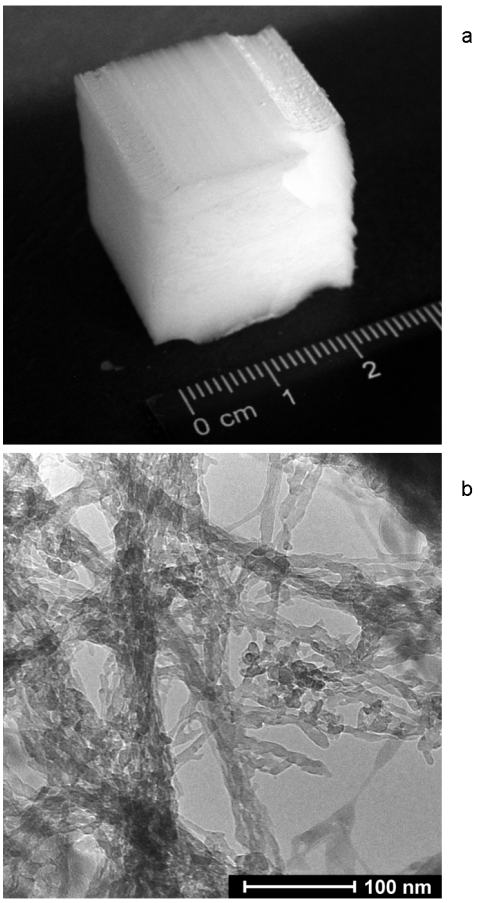

Fig. 1. (a) Photo of grown native nanostructured oxyhydroxide of aluminium monolith sample; (b) TEM image of the structure of the native NOA sample at 80 K.

At the Mie scattering range (ii) we have measured scattering indicatrix at 633 nm presented at Fig. 2b with He–Ne laser source. The experimental setup and measurement technique for porous samples are presented in [3]. The experimental data have shown that the NOA pellet belongs to so-called Lambert-type scattering sources: the measured indicatrix (dots) can be described with cosine angular distribution (solid curve). The integrated total transmittance in the forward hemisphere was 17±1 %. The magnitude depends on the selected point and laser beam radius. The estimates have shown that only about 0.01 % of the input photons propagate into the spatial angle corresponding to free diffraction of the laser beam without the sample. Thus almost 99.95 % of the transmitted photons belong to so-called diffusive ones that mani-

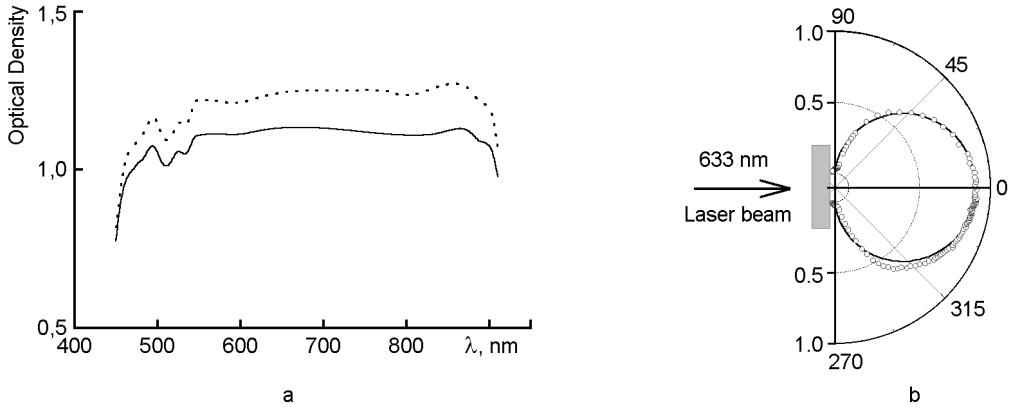

Fig. 2. (a) Spectral optical density of the NOA pellet for the different points of the sample, (b). Scattering indicatrix of the pellet at 633 nm (dots), Lambert type model (solid line).

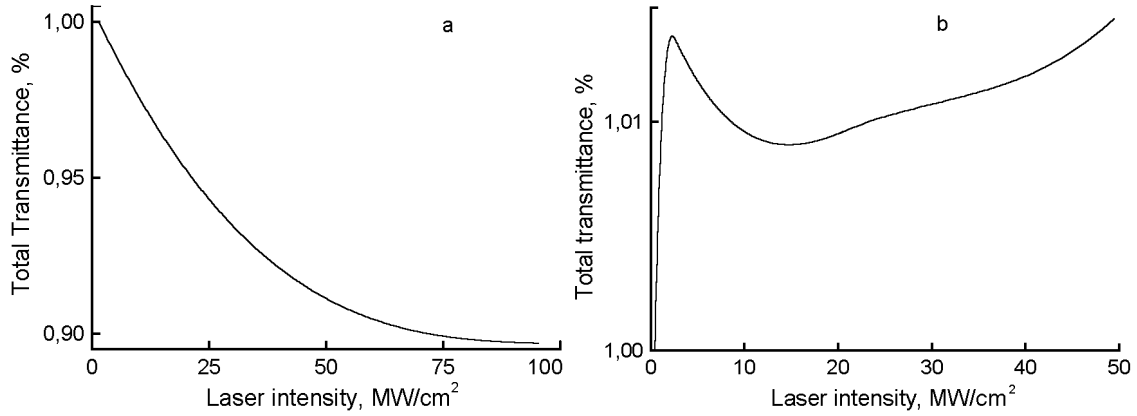

Fig. 3. The photoinduced variation of the total transmittance of the NOA pellet normalized on linear one versus the peak laser intensity at wavelength 1064 (a) and 532 (b) nm. The pulsewidth is 30 ps (FWHM) at 532 nm.

fests multiple scattering phenomena at the developed nanofibrils network in the sample.

We have studied photoinduced variation of the total transmittance of the NOA pellet with single pulse laser radiation of mode-locked Nd:YAG laser at the fundamental (1064 nm) and second harmonic (532 nm, 30 ps FWHM pulsewidth) wavelengths. The approach was verified with NLO diagnostics results of both organic and inorganic nanostructured subsystems in different kinds of matrices (single [4, 5] and liquid [6] crystals, porous layers [7, 8] etc.). The experimental setup is described in [7], the experimental technique implementation peculariti es for scattering samples is presented in [9]. The sample was mounted on the photodiode input aperture (∅~7 mm), the typical laser beam spots at the sample plane were 0.5–0.8 mm (FWHM). We can suggest that the photodiode collect almost all photons transmitted to the forward hemisphere of the sample. The variation of the transmitted signal can be explained in terms of three factors changes: (a) photoinduced absorption/saturation, (b) scattering in backward hemisphere, especially coherent backward scattering opposite to the incident beam, (c) essential redistribution of the scattering indicatrix in the forward hemisphere.

The total transmittances of the NOA pellet versus peak laser intensity are presented at Fig. 3 for 1064 nm (a) and 532 nm (b) excitation wave lengths. In order to avoid impact of the sample optical inhomogeneity dealing with different sample points and laser beam radii we normalized the experimental data on the transmittance at the initial intensity (less 1 MW/cm^2) range. Thus we have obtained the reproducible NLO data for the different spots and geometries of the experiments.

In the range of moderate peak laser intensities up to 100 MW/cm^2 we have not

observed the impact of the (c) factor. In the realized approach of the registration we can not separate the impacts of the (a) and (b) factors and we are going to describe the effects as effective photoinduced absorption/saturation phenomena in terms of the imaginary part of the effective cubic NLO susceptibility $Im(\chi^{(3)})$ as the simplest model [10].

The NLO response of the NOA at 1064 nm is similar to the porous layers of nanostructured TiO_2 [7] and Si [8] ones. We have observed efficient photoinduced extinction enhancement (see Fig. 3a) with the laser intensity growth that starts to saturate at 60 MW/cm^2. In the initial intensity range (~10 MW/cm^2) the effective NLO response $Im(\chi^{(3)})$ is about $1.7 \cdot 10^{-9}$ esu that is an order of magnitude higher the corresponding one at 80 MW/cm^2 — $Im(\chi^{(3)}) \sim 1.1 \cdot 10^{-10}$ esu.

Excitation of the sample at 532 nm changes the character of the NLO response (see Fig. 3b) that had nonmonotonic character versus the peak laser intensity. The excitation wave length is in the complex band of the reduced extinction of the sample (see Fig. 2a). The described response is typical to resonant excitation of some defect states of the NOA. The initial sharp photoinduced increase ($Im(\chi^{(3)}) \sim -2.1 \cdot 10^{-9}$ esu) of the total transmittance, that gains the peak ~1 % at the intensity about 2.3 MW/cm^2, changes to steep decrease ($Im(\chi^{(3)}) \sim 1.9 \cdot 10^{-10}$ esu) up to 15 MW/cm^2 with consequent enhancement of the samples transmittance ($Im(\chi^{(3)}) \sim -3.0 \cdot 10^{-11}$ esu).

Taking into account the porosity of the pellet we can state that NOA nanofibrils have efficient NLO response $|Im(\chi^{(3)})| \sim 10^{-7}$ esu due to the picosecond range laser pulses self-action phenomenon. The magnitude of the effect is comparable with NLO response of the porous titanium dioxide and porous silicon layers and it is a few orders of magnitude higher in comparison with the response of the bulk one. The effect can be attributed to the giant NLO response manifestation due to the resonant excitation of the defect states at the developed NOA surface.

For the first time the efficient NLO response of the ultraporous NOA structure was observed. The response demonstrates typical features of the resonance excitation at 532 nm (extinction bleaching saturation) and two-photon one at 1064 nm (extinction enhancement) within picosecond range laser pulse excitation. The effect can be utilized for surface states diagnostics and their interaction with adsorbates. The different kinds of the response provide possibility of the adsorbate state smart control via photoinduced giant local fields in the NOA matrix for the visible-IR-THz domain spectroscopy and random lasing applications.

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References

1. J.-L.Vignes, C.Frappart, Th.Di Costanzo et al., *J. Mater. Sci.*, **43**, 1234 (2008).
2. A.N.Khodan, P.N.Martinov, R.Sh.Askhadullin et al., Corrosion: Materials, Protection, 2, 6 (2009) [in Russian].
3. A.Borshch, M.Brodyn, V.Gayvoronsky et al., *Ukr. Fiz. Zh.*, **49**, 196 (2004).
4. I.Pritula, V.Gayvoronsky, M.Kopylovsky et al., *Functional Materials*, **15**, 420 (2008).
5. I.Pritula, V.Gayvoronsky, Yu.Gromov et al., *Opt. Comm.*, **282**, 1141 (2009).
6. V.M.Pergamenshchik, V.Ya.Gayvoronsky, S.V.Yakunin et al., *Functional Materials*, **13**, 681 (2006).
7. V.Gayvoronsky, A.Galas, E.Shepelyavyy et al., *Appl. Phys. B*, **80**, 97 (2005).
8. V.Ya.Gayvoronsky, M.K.Kopylovsky, Yu.V.Gromov et al., *Las. Phys. Lett.*, 5, 894 (2008).
9. V.Gayvoronsky, S.Yakunin, V.Nazarenko et al., *MCLC*, **426**, 231 (2005).
10. A.A.Borshch, M.S.Brodyn, V.Ya.Gayvoronsky, *Proc. SPIE*, **5024**, 128 (2003).

Оптична та нелінійно-оптична характеризація наноструктурованого оксигідрооксиду алюмінію

В.Я.Гайворонський, М.А.Копиловський, Є.О.Вишняков, А.М.Ходан, J.-L.Vignes, М.М.Есаулков, О.П.Шкуринов

Проведено дослідження спектрів дифузного пропускання, індикатриси розсіювання та нелінійно-оптичного (НЛО) відгуку при збудженні лазерними імпульсами пікосекундного діапазону нового функціонального матеріалу — ультрапористого наноструктурованого оксигідрооксиду алюмінію (НОА). Спостерігався внесок двох механізмів фотоіндукованого зростання екстинкції на фундаментальній довжині хвилі випромінювання 1064 нм Nd:AIГ лазера, котрий є подібним до НЛО відгуку пористих шарів діоксиду титану та кремнію. На довжині хвилі другої гармоніки лазера спостерігався немонотонний характер НЛО відгуку з типовим проявом ефекту зростання пропускання внаслідок резонансного збудження поверхневих станів НОА. Виявлені ефекти можуть бути використані для керування оптичними методами станом адсорбованих на поверхні НОА молекул для спектроскопічних застосувань та для отримання випадкової лазерної генерації у середовищі, що сильно розсіює світло.