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Fundamental principles for the development of new functional nanocomposite materials based on oxide 3D nanostructures for applications in THz optics and information transfer

A. Kanaev¹, A. N. Khodan², K. I. Zaytsev³, V. N. Kurlov⁴

¹ Laboratoire des Sciences des Procédés et des Matériaux (LSPM), CNRS, Université Paris 13, Villetaneuse, France

² Frumkin Institute of Physical Chemistry and Electrochemistry (IPCE), RAS, Moscow, Russia

³ Prokhorov General Physics Institute (GPI), RAS, Moscow, Russia

⁴ Institute of Solid State Physics (ISSP), RAS, Chernogolovka, Russia

E-mail: andrei.kanaev@lspm.cnrs.fr; anatole.khodan@gmail.com

Abstract – The purpose of this work is development of the solid-state materials possessing a small absorption combined with sufficient refraction index in the THz range. The main criteria, which were used for the material selection, were quite simple: inorganic compound with strong chemical bonds, stoichiometric composition, small concentration of delocalized charge carriers and sufficient polarizability over THz frequency range. It is obvious, that inorganic materials match these criteria in the greatest degree and, first of all, stable oxides with a high fusion temperature: Al₂O₃, SiO₂. In this work we studied monolithic nanofibrous alumina for the THz frequency range, which synthesis process was previously developed [1-5].

Keywords – *nanomaterials, 3D nanostructure, mesoporous materials, aluminium oxyhydroxides, ultraporous alumina, nanocomposites, dielectric properties, THz optics*

I. INTRODUCTION

The choice of materials for THz optics is rather limited, only some polymer materials even porous are used now for this purpose: polyethylene, polytetrafluoroethylene, polypropylene and others. The most common disadvantage of polymer systems is their rather high absorption over the THz frequency range, caused by singularities of chemical composition and intra- and intermolecular hydrogen bonds. The presence of the unshared electronic pairs in a substance, as well as equal availability of the molecular water, and free and loosely coupled charge carriers; all this a priori should enhance the interaction with an electromagnetic radiation and lead to the increment of losses. Probably, it is the reason of why the metallic mirrors are still used for low-loss optical systems in the THz frequency range.

Currently, there are no systematic studies of dielectric properties of porous 3D nanostructures based on hydroxides and oxides of aluminum in the THz range. In this work we report on first studies of monolithic nanofibrous alumina in the THz frequency range.

II. EXPERIMENTAL

New functional materials and nanocomposites were developed on the basis of the original laboratory technology (LT), which has been developed for more than 20 years in the framework of scientific cooperation between LSPM CNRS and

IPCE RAS [1-5]. Currently LT allows to obtain highly porous monolithic blocks (PMOA), having a shape with a given cross-section from ~ 1 cm² to < 100 cm² and a height from 0.5 cm to 20 cm. The 2D structure of PMOA consists of alumina nanofibrils of a diameter ~4 – 7 nm and a length of ~120 – 250 nm. Annealing of PMOA in the temperature range of 400 – 1700 °C leads to the isotropic dimensions reduction while samples are not destroyed and retain the porous structure. By varying the annealing conditions, one can control the material mass density in the range from 0.02 to 3 g/cm³, specific surface area from 300 to 1 m²/g, and open porosity from 99.3 to 25% (Fig. 1a). To describe the evolution of the 3D structure of PMOA during the annealing process, we proposed a physical model that describes the experimental results for annealing temperatures from 100 °C to 1700 °C with a good quantitative agreement [5].

The simplest effective media models using Maxwell-Garnett, Bruggeman and Landau-Lifshitz-Looyenga equations was applied to describe the optical properties of the PMOA materials in the THz range, and good agreement with the experimental results was achieved.

Presently we are conducting exploratory joint studies with the participation of laboratories of the GPI RAS and ISSP RAS on novel functional materials based on 3D oxide nanostructures and nanocomposites. The general goal is developing materials with given and controlled electrodynamic properties for the GHz, THz, IR optics and devices.

An important area of the current research is the development of methods for creating functional 3D hybrid nanostructures and nanocomposites by chemical modification of PMOA surface. The surface modification of PMOA can be carried out from both gas and liquid media. With the purpose of functionalization of the materials properties, various methods of the structural and chemical modification have been developed: by applying of metalorganic compounds (siloxanes, phthalocyanines, oxyquinolates), impregnation with nanoparticles <10 nm of TiO₂, ZrO₂, NiO₂, CeO_x, etc. [6-7]. A particular attention was paid to the interdisciplinary studies of functional heterostructures based on PMOA – monophthalocyaninates of transition metals and sandwich complexes of rare-earth elements [8]. The IPCE RAS has accumulated a vast experience in the synthesis and study of properties of supramolecular materials, establishing patterns of

complex formation reactions, which allow high-yield complexes of a given structure with desirable functional characteristics. Original results have been obtained indicating an enhancement of the nonlinear optical properties of supramolecular ensembles, which opened up prospects for creating new materials for optical limiting, dynamic holography, telecommunication, etc.

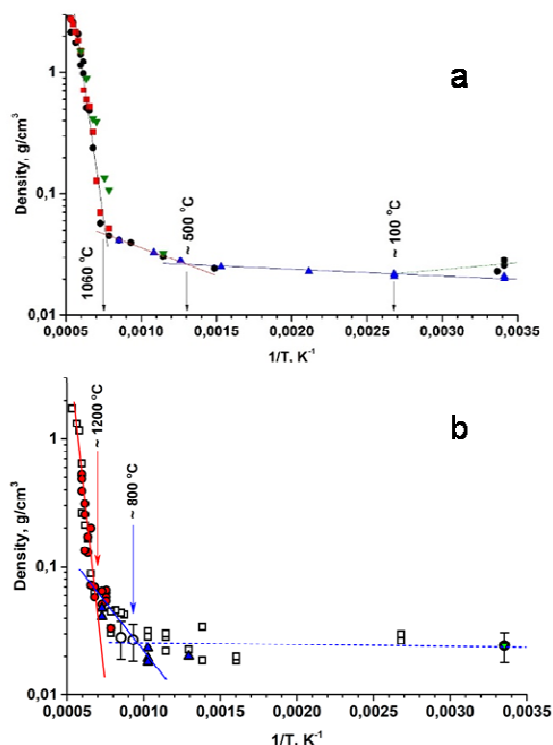


Fig. 1. Density of the samples as a function of the annealing temperature (isochronous annealing time 4 hours). The different series of measurements are indicated with different markers: a) NOA samples [7]; b) NOAM samples.

Our systematic studies of the dielectric properties of samples of monolithic highly porous aluminium oxyhydroxides and composite nanostructures began in 2018. Samples in form of plane-parallel plates were studied using THz pulse spectroscopy methods and original THz pulsed spectrometer, developed and assembled in the Laboratory of Submillimeter Dielectric Spectroscopy of GPI RAS [9].

The spectroscopic studies of PMOA samples were carried out using the passage of short THz pulses through a sample with different orientations of the THz electric field relative to the direction of growth of PMOA, along which the texture formation is associated with the predominant growth of alumina nanofibrils. Based on the analysis of the complex amplitude of the THz field passing through a sample and empty cell in the spectrometer (Fig. 2), the complex dielectric constant and complex refractive index were restored, for which an original method of analysis and related software were described in Refs [10-13]. The results in Fig. 3 indicate that PMEA materials are characterized by rather low absorption of THz radiation in a wide frequency range. Its effective refractive index is significantly lower than that of the homogeneous sapphire [13], which is due to a high porosity of the material. Considering two orthogonal polarizations of the THz radiation relative to the direction of orientation of the sapphire nanowires, one can note a significant anisotropy of the optical properties about 10... 40%, depending on structural properties of samples and frequency of electromagnetic radiation.

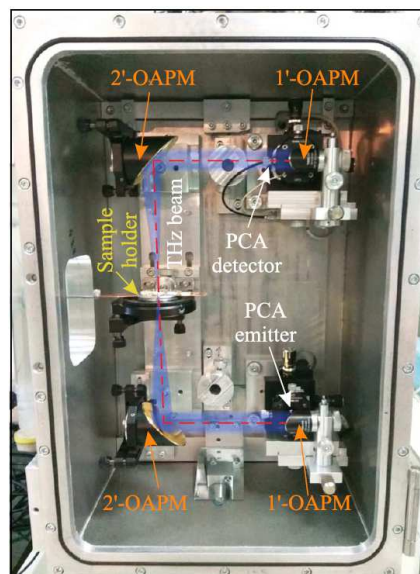


Fig. 2. Laboratory spectrometer using generation and detection of THz pulses in LT - GaAs based photoconductive antennas and equipped with a vacuum measuring chamber (pressure 10^{-3} mbar). Operating frequency range: 0.05 to 4.5 THz, spectral resolution 0.005 THz [8].

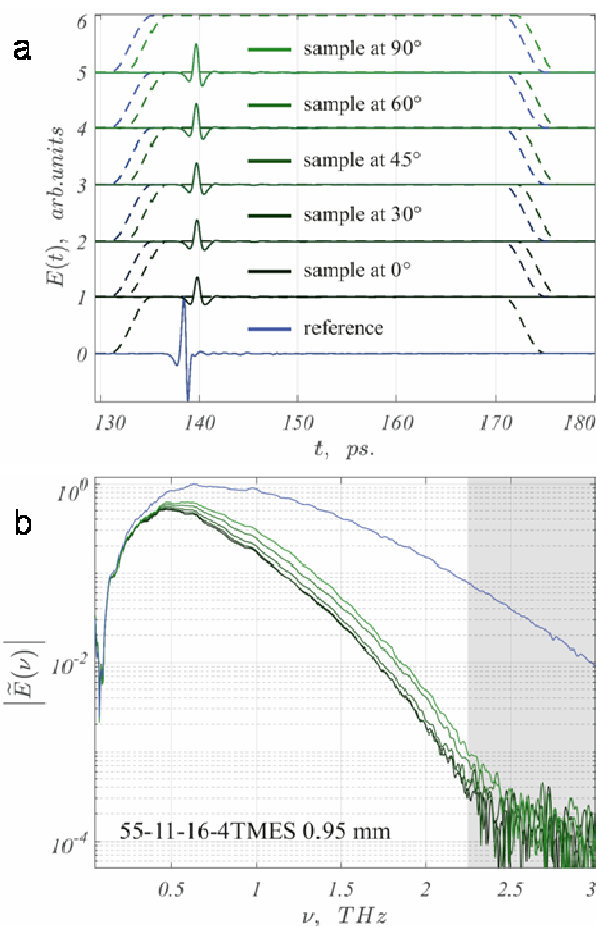


Fig. 3. Results of THz pulsed spectroscopy of porous Al_2O_3 : reference THz pulse transmitted through the empty cell of the spectrometer, and THz pulses transmitted through the sample with different polarization of the incident radiation (a) and amplitude of the Fourier spectra of these pulses (b).

The results of preliminary studies indicate a promise of the chosen direction related to a principal possibility of creating novel PMOA based materials for THz optics. Such porous media and nanocomposites are extremely interesting objects for dielectric spectroscopy studies. The most important stages of the related research towards novel materials for THz optics and information transfer devices [12] include studies of elementary electromagnetic dipole excitations of a porous medium, establishing correlations between the dielectric response and structure of the material and, consequently, the relations with key parameters of the technological process of its manufacturing.

We notice an importance of studies of mechanical properties of functional materials based on PMOA. A successful use of highly porous functional 3D nanomaterials in technical devices is impossible without studying their strength and resistance to external factors under operating conditions. This work will be conducted in Derzhavin TSU in the "Nanotechnologies and Nanomaterials" Research and Education Center, which has accumulated vast experience in the field, using traditional and original patented methods of studying fine features of the materials structure, crystalline phase, mechanical and thermal properties.

IV. CONCLUSIONS

The new nanocomposite oxide systems were developed with properties designed for applications in the THz-GHz optics. The materials based on monolithic nanofibrous alumina open up the possibility for linear and non-linear optics, heterogeneous macro-ordered materials and metamaterials.

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