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Study of Second Harmonic Generation in KDP/Al_2O_3 Crystalline Nanocomposite

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Crystalline nanocomposite KDP/Al_2O_3 was obtained by growth of KDP nanocrystals inside nanopores of amorphous alumina matrix (Al_2O_3) with pores diameter of 35 nm. Performed atomic force microscopy and X-ray diffraction analysis confirmed that Al_2O_3 matrix is filled up with a tetragonal phase KDP nanocrystals in preferred crystallographic orientation [100]. The nonlinear optical response was studied by means of second harmonic generation via the Maker fringe technique employing picosecond laser pulses at wavelength of 1064 nm. The polarization dependent second harmonic generation response was observed mainly due to the macroscopic crystalline structure anisotropy of KDP/Al_2O_3 nanocomposite. The investigation of such type of nanocomposites which combine nanoscale nonlinear optical materials has a great importance since they may improve the performance of entire system.

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1. Introduction

The physical properties of composite materials can be controlled and optimized over a wide range of values by changing the composition type, structure and size of the constituent elements. The particular interest is devoted to the preparation of composite materials from dielectric materials such as alumina, silica, and polymers, which contain high density of uniform sized pores in the diameter range between few nm and few μm and in the length up to hundreds of μm (so-called nanoporous matrices or membranes — see, for example, www.smartmembranes.de/en/products). Applying liquid phase processes these pores can be easily filled up with metals, semiconductors, dielectrics or liquid crystals [1–4]. In this way the created composite may combine the particular properties of both nanoporous matrix and embedded nanoscale material as well as possess the possibility of their tuning.

It is noteworthy that besides highly efficient single-crystal nonlinear optical (NLO) materials [5–8] new type can be created just by filling the pores in porous matrix with NLO materials. In this case the skeleton can be designed to provide phase matching, while the material filling the pores will contribute mainly to the second harmonic generation (SHG) efficiency [9]. Hence, the efficiency of nanocomposite can be increased by filling with the NLO nanocrystals in the specified direction of crystalline orientations inducing the anisotropy of entire crystalline nanocomposite. We already have initiated the work on the creation of crystalline nanocomposites with tailored anisotropy, which will give the possibility of directional crystallization forming of nanocrystals in pores of matrices [10, 11]. In addition, it was shown that KH_2PO_4 (KDP) crystals with incorporated nanoparticles of aluminum oxyhydroxide possess high optical quality and homogeneity and the enhancement of nonlinear refractive index and inversion of its sign as well as the second harmonic generation efficiency enhancement were observed in comparison with nominally pure KDP crystals under excitation of pico- or nanosecond laser pulses [12, 13]. The dielectric properties of KDP filled porous alumina nanocomposite thin films have been already studied [14] but there is no report on their NLO properties. Herein, we report on the fabrication of nanocomposite material in which well-known and wide-used NLO material KDP is inserted into alumina nanopores. The microstructure and NLO properties of KDP/Al_2O_3 nanocomposite were studied and obtained results are presented in this paper, which is rather a pioneer approach possessing both scientific and practical importance.

2. Experimental part

The nanocomposites KDP/Al_2O_3 were obtained by growth of KDP nanocrystals inside nanopores of amorphous alumina matrix (Al_2O_3). The growth method was based on the controlled slow temperature descending of saturated aqueous solution of potassium dihydrogen phosphate [10]. The alumina nanoporous matrices with

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thickness of 0.1 mm, pores diameter 35 nm and their period of 100 nm were purchased from SmartMembrane Ltd. Company.

SHG measurements were performed by means of the rotational Maker fringe technique in the transmission scheme for the linear-polarized fundamental laser beam (Fig. 1). An y-cut crystalline quartz plate was used as a reference material for these measurements and data processing. The output beam of a mode-locked Nd:YAG/YVO_4 laser (EKSPLA) generating at λ = 1064 nm with 30 ps pulse duration and 10 Hz repetition rate was employed as a fundamental beam. The input energy of laser pulses was controlled by laser power/energy meter LabMax TOP (COHERENT) to be 140 μJ. The detailed setup description can be found elsewhere [15].

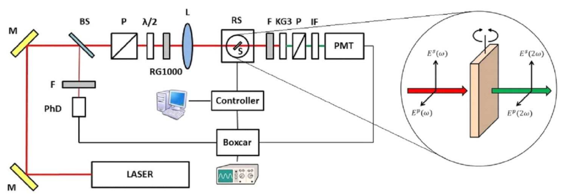

Fig. 1. Setup for the SHG measurements: M — mirrors, BS — beam splitters, PhD — photodiode, P — Glan polarizers, $\lambda/2$ — half wave plate, RG1000 — filter RG1000, L — lens, RS — rotation stage, S — sample, F — neutral density filters, KG3 — KG3 filter, IF — interference filter, PMT — photomultiplier tube.

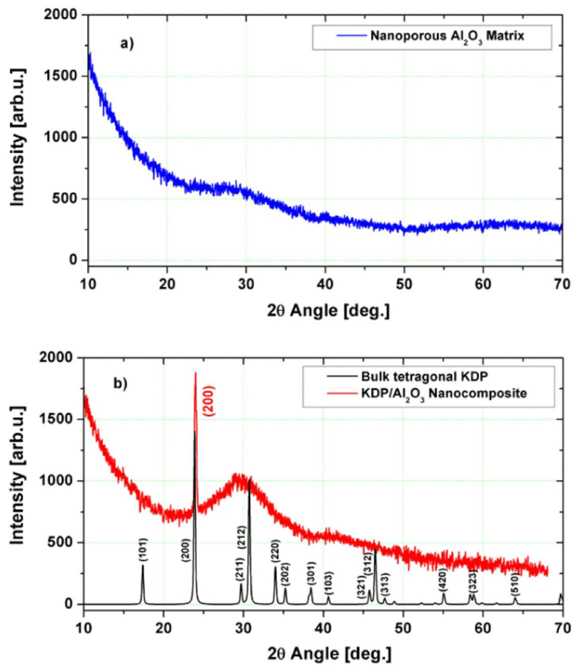

Fig. 2. XRD patterns for: (a) nanoporous Al_2O_3 matrix and (b) KDP/Al_2O_3 crystalline nanocomposite and bulk tetragonal KDP.

3. Results and discussion

3.1. XRD crystalline structure analysis

The crystalline constituents in nanocomposite can have higher thermal or/and chemical stability while the predefined anisotropy of their crystalline orientation induced by corresponding growth procedure may improve some crucial characteristics. The crystalline structure and composition of prepared KDP/Al_2O_3 crystalline nanocomposite was studied by means of X-ray diffraction (XRD) technique and compared with pure alumina matrix and bulk KDP (Fig. 2). There is no characteristic peak in XRD pattern corresponding to crystalline phase of nanoporous alumina, hence it can be concluded that it is amorphous, while in the XRD pattern of KDP/Al_2O_3 nanocomposite the clear sharp peak, which corresponds to [100] direction (reflection from (200) plane) of tetragonal phase of bulk KDP appears. As it can be concluded, the Al_2O_3 is filled up with a KDP material in a tetragonal crystalline phase with the preferred crystalline orientation [100] in the direction perpendicular to surface of alumina plate.

3.2. AFM surface topology analysis

The surface topology of the samples was examined by using AFM (NT-MDT) in semicontact mode. In Fig. 3 the images obtained for pure alumina matrix and KDP/Al_2O_3 nanocomposite are collected. The alumina matrix represents an obvious structure — the array of uniform nanometer sized parallel pores in hexagonal arrangement with the parameters (pores period and diameter) about to the reported by manufacturer ones. The surface topology of KDP/Al_2O_3 crystalline nanocomposite is rougher and nanopores are hardly visible since they are filled up with KDP nanocrystals (Fig. 3c,d). This confirms that the liquid solution has penetrated into the alumina nanopores.

3.3. SHG measurements

The SHG technique is very sensitive to the presence of NLO media even in small quantities since it quadratically depends on laser intensity. However, this media should be noncentrosymmetric in order to demonstrate SHG response. The dependence of SHG intensity in KDP/Al_2O_3 crystalline nanocomposite on angle of sample rotation (zero angle corresponds to normal beam incidence) for s-polarized laser beam is shown in Fig. 4a. Obtained SHG response confirms the presence of KDP in nanopores of alumina matrix.

The intensity of SHG was measured and compared to that from a quartz plate and the value of quadratic NLO susceptibility was estimated using the following equation [16]:

$$\chi^{(2)} = \chi^{(2)}_{Quartz} \left(\frac{2}{\pi}\right) \left(\frac{l^{coh}_{Quartz}}{d}\right) \left(\frac{I^{2\omega}}{I^{2\omega}_{Quartz}}\right)^{1/2},$$

where $\chi^{(2)}_{Quartz} = 1.0\,\text{pm/V}$, $l^{coh}_{Quartz} = \frac{\lambda}{4\bullet|n_{2\omega}-n_{\omega}|} = 21\,\mu\text{m}$ is coherent length of quartz, d is sample effective thickness, $I^{2\omega}$ and $I^{2\omega}_{Quartz}$ are the SHG intensities from the sample and quartz under the same conditions, respectively. The value of quadratic NLO susceptibility was found to be $\chi^{(2)} = 2.4\times10^{-3}$ pm/V, which is two orders of magnitude less than of bulk KDP [17] mostly due to the fact that in $\chi^{(2)}$ calculations it was taken into account that the nanopores are totally filled up with KDP and light scattering was neglected. It is noteworthy that the nanoporous alumina is matt material, for the further using in optics or nonlinear optics its optical transmittance should be improved.

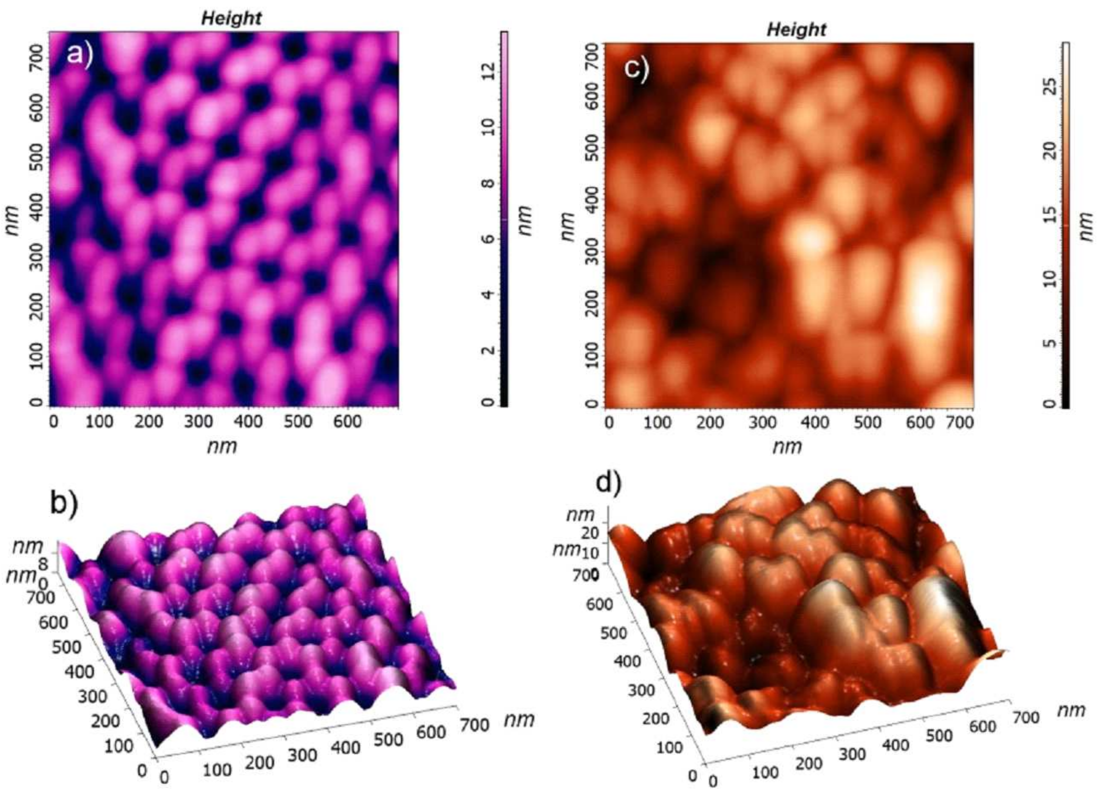

Fig. 3. 2D and 3D AFM topology images of nanoporous Al_2O_3 matrix (a, b) and KDP/Al_2O_3 crystalline nanocomposite (c, d).

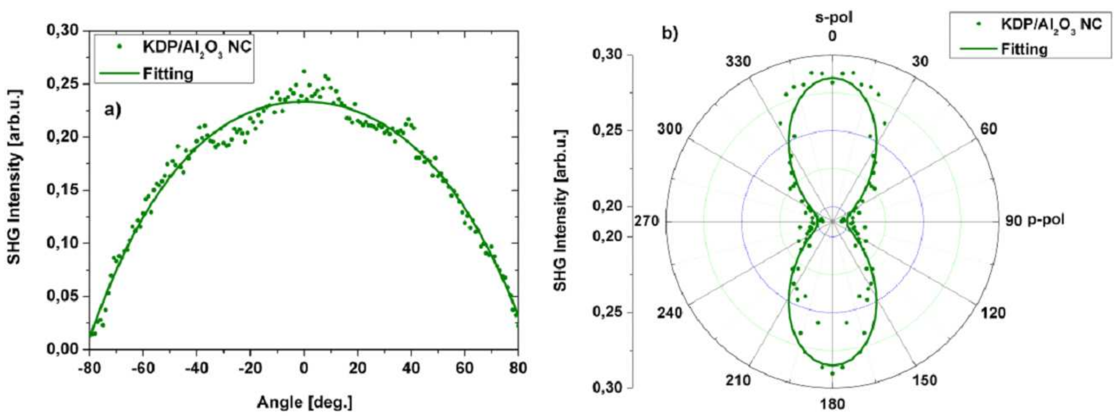

Fig. 4. (a) SHG intensity as a function of incident angle in KDP/Al_2O_3 nanocomposite at the s-polarized laser beam; (b) polar plot of the polarization dependent SHG signal from KDP/Al_2O_3 nanocomposite.

In Fig. 4b the dependence of SHG intensity on polarization of incident laser beam from KDP/Al_2O_3 crystalline nanocomposite in polar plot is given. As it can be noticed, the polarization dependent anisotropy of SHG signal takes place probably due to macroscopic symmetry (crystallographic features) of KDP nanocrystals inside pores of alumina. Therefore, our further research stage will be concentrated on the simulation and maximization of NLO response in KDP/Al_2O_3 crystalline nanocomposite.

4. Conclusions

KDP nanocrystals were successfully grown inside nanopores of Al_2O_3 matrix from saturated solution due to capillary forces with a preferred [100] orientation as it is confirmed from AFM and XRD analysis. The noticeable NLO response in KDP/Al_2O_3 crystalline nanocomposite was observed via SHG measurements using the Maker fringe technique. The induced anisotropy of SHG response in KDP/Al_2O_3 crystalline nanocomposite is caused by its macroscopic crystallographic symmetry features. SHG method is very sensitive way for the investigation of nanocomposites which are comprised of NLO materials. The concept of nanocomposites filled up with active nanostructures with tailored anisotropy of crystalline orientation may open new class of material interesting for electro-optic and photonic applications.

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