Physica E 64 (2014) 1–6

Contents lists available at ScienceDirect

Physica E

journal homepage: www.elsevier.com/locate/physe

Nonlinear optical features of δ-BiB_3O_6/PVA polymer nanocomposites deposited on aluminum-doped zinc oxide substrates containing Ag nanoparticles

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HIGHLIGHTS

- Complex polymer silver BiB3O6 nanocomposites are synthesized.
- Z-scan and second harmonic generation show existence of some maximum at 20 nm sizes.
- Principal role of surface plasmon resonances interacting with the localized states is shown.

ARTICLE INFO

Article history:
Received 2 June 2014
Received in revised form
13 June 2014
Accepted 16 June 2014
Available online 4 July 2014

Keywords:
Nanocomposite
Optical property
Borate nanocrystallites

ABSTRACT

For the first time the Z-scan measurements and second harmonic generation of δ-BiB_3O_6:Pr^{3+} large-size nanocrystallites embedded into the polyvinyl alcohol (PVA) polymer matrices and deposited on AlZnO substrates decorated with Ag NP were studied. The comparison of the second and third order NLO is presented. The Z-scan measurements were done by 5 ns Nd:YAG laser and the second harmonic generation was measured using the 25 ns Nd:YAG laser with frequency repetition about 10 Hz. The measurements have shown that both second as well as third-order susceptibilities are sensitive to the sizes of the Ag NP deposited on the AlZnO substrate. The obtained results confirm a principal role of the Ag NP on the output nonlinear optical properties which may be a consequence of the contribution of the low-dimensional nano-trapping levels.

1. Introduction

The studies of borate nanoparticles embedded into the polymer matrices present a substantial interest due to their optically operated nonlinear optical susceptibilities. For example $CsLiB_6O_{10}$ crystallites embedded into the olygoether photopolymer matrices are new materials for the acoustically induced nonlinear optics [1,2]. Such prepared structures contain the oxide nanoparticles embedded into the polymer which serves as matrix and the interfaces separating the nanoparticles and polymers play here a crucial role.

Interaction of light with nanocomposites reveals novel optical phenomena indicating unrivalled optical properties of these materials. The linear and nonlinear optical response of metal nanoparticles is specified by oscillations of the surface electrons in the Coulomb potential formed by the positively charged ionic core. This type of excitation is called the Surface Plasmon (SP). In 1908 Mie proposed a solution of Maxwell's equations for spherical particles interacting with plane electromagnetic waves, which explains the origin of surface plasmon resonance (SPR) in the extinction spectra and colouration of metal colloids [3].

Usually the nonlinear optical studies were done for the organic chromophores incorporated into the polymer matrices using the spin coating technique [4–6]. However, these compounds are not stable with respect to external laser light and their nonlinear optical susceptibilities decrease with the irradiation times.

In Ref. [7] observation of high-order optical nonlinearities in our recently developed photopolymerizable semiconductor CdSe quantum dot (QD)-polymer nanocomposite films at various volume

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http://dx.doi.org/10.1016/j.physe.2014.06.015
1386-9477/

fractions of CdSe was reported. Moreover, using the uniformly cured polymer nanocomposite films, it was observed the third- and fifth-order nonlinear optical effects in closed-aperture Z-scan measurements by which it was found that saturable nonlinear absorption (light-induced transparency) and large negative nonlinear refraction were induced.

There is a growing interest in the incorporation of inorganic nanoparticles into polymers to improve various functional properties (such as mechanical, thermal, optical, magnetic, and electrical properties). However, the ultimate properties of nanocomposites are affected by a large number of factors including the microstructural distributions that are generated during nanocomposite processing. While significant work has been done on preparation and properties of polymer nanocomposites, the interrelationship among processing, morphology, and functional properties of nanocomposites is complex and needs further elucidation. Furthermore, the effective utilization of nanoparticles in polymers depends strongly on the ability to disperse the nanoparticles uniformly throughout the polymeric matrices especially without reducing their aspect ratios [8].

In the present paper we will try to use the possible enhancement of the second and third-order nonlinear optical properties due to use of Ag NP deposited on the Al–ZnO substrate for the large-size borate nanocrystallites embedded into the polymer matrices. Following the previous works on the nonlinear optical properties of the Ag NP [9–11] and of the borate nanocomposites [12,13] one can expect a possibility to achieve some enhancement both of the second as well as third order susceptibilities.

For this reason we deposited the polymer/borate nanocrystallites composites on several substrates containing Ag NP having different sizes.

2. Experimental method

The synthesis of the AgNP deposited on the Al–ZnO substrate was performed similarly to the modification of AuNPs described in Ref. [14]. This time, AgNP-attached AZO substrates were prepared using silver colloid solutions (containing 10, 20 and 40 nm AgNPs; Sigma-Aldrich), 3-aminopropyltrimethoxysilane (APTMS; Sigma-Aldrich) and aluminum-doped zinc oxide (AZO) coated glass plates (Geomatec Co.Ltd., Japan). As the actual procedure, initially, a piece of an AZO plate (1.0 cm $\times$ 1.0 cm) was washed under sonication, first in acetone, then in ethanol, and finally in pure water, and dried with N_2 gas. Next, it was treated at 70 °C for 1.5 h in the mixture of water, ammonium hydroxide (30%) and hydrogen peroxide (30%) (5:1:1, v/v), and followed by washing with pure water. After drying with N_2 gas, the AZO plate was immersed in the mixture of ethanol and APTMS (100:2, v/v) overnight at 28 °C to prepare an APTMS-modified AZO plate.

It was washed with ethanol to remove residual APTMS and dried with N_2 gas. Finally, the APTMS-modified AZO was immersed in a 10 nm (20 or 40 nm) silver colloid solution for 2 h at 28 °C. After washing with pure water and drying with nitrogen gas, the AgNP-decorated AZO was obtained.

The AFM images of the Ag NP possessing the sizes 10 nm, 20 nm and 40 nm modified on AZO are presented in Fig. 1. For the AFM measurements in air, a commercially available apparatus, MultiMode AFM (Bruker Corp.) was used with a cantilever, SSS-NCHR (Nano World AG), whose nominal spring constant and resonance frequency were 42 N/m and 330 kHz, respectively. The images were acquired in TappingMode. One can see clearly that the increasing Ag NP sizes favor also the substantial changes of the inter-particle distances as well vary partially their topology.

The polymer composites consist of poly(vinyl alcohol)—PVA containing particles of δ-BIBO doped with praseodymium (7.5 at%). This content has demonstrated the highest nonlinear optical response. The composites were prepared by means of the solvent method [15,16], where the main idea was to disperse the polymer and filler in the same solvent, which in this process was water. This method was modified by one additional step, namely, the filler was dispersed in the water solution of a surfactant in order to improve uniformity of the filler dispersion in the matrix volume. To perform this process the following substrates were used: poly (vinyl alcohol) PVA 18GP (SHIN ETSU CHEMICAL CO.) as a matrix, polyethylene glycol PEG 5000 (ALDRICH) as the surfactant, distilled water and nonlinear optical δ-BiB_3O_6:Pr^{3+} 7.5% particles prepared by means of the sol–gel method [17]. In the first step aqueous solutions of PVA (10.0 wt%) and PEG (2.0 wt%) were prepared. 10 g of PVA was dissolved in 90 ml of water and then solution was intensively stirred by a magnetic stirrer with mutual heating at 90 ± 5 °C with 500 rpm for 2 h. At the same time aqueous solution of PEG was prepared by stirring 8 ml of water and 2 g of surfactant powder at room temperature for 1 h. In the next step 0.2 ml of PEG solution and 0.15 g of filler were mixed together. Then solutions of matrix and filler were mixed intensively in homogenizer (TOPEX) with 10,000 rpm for 10 min. In the last step, composite solution was deposited onto glass substrate and was dried at room temperature for 4 days.

The polycrystalline powder samples of δ-BIBO:Pr^{3+} (7.5 at% of Pr substituted for Bi) were prepared by means of the Pechini method through the citric way. The metal oxides of Bi and Pr were dissolved in a concentrated (65% vol.) nitric acid under stirring and heating at 60 °C. Because the additional polymerizing agent was not included and due to boron volatility at higher temperatures, an excess of boric acid (10% molar) was required and charged into solution. To complex the metal ions an excess amount of citric acid was used (with molar ratio 4:1 with respect to Me^{3+}). The solution was kept at 120 °C for 12 h to evaporate the solvent and to initiate the polymerization. After gelation the temperature of furnace was raised to 650 °C and the pyrolysis process lasted 30 h. After intermediate grounding and mixing, the powders were calcinated for 65 h at 700 °C and the polycrystalline samples of δ-BIBO:Pr^{3+}(7.5%) were obtained. In Fig. 2 scanning electron microscopy images of the prepared nanopowders are shown.

The absorption spectra are presented in Fig. 3. One can see that there are some differences in the level of the absorption for the different Ag NP sizes.

3. Experimental nonlinear optical methods

3.1. The Z-scan method studies

The Z-scan technique is a method which can rapidly measure the nonlinear index n_2 nonlinearity and the non-linear absorption coefficient $\Delta\alpha$ in solids, liquids and liquid solutions [18,19]. The Z-scan method is used to measure both NLA and NLR in the “closed” and “open” methods, respectively. As nonlinear absorption can affect the measurement of the nonlinear index the open method is typically used in conjunction with the closed method to correct the calculated value.

The experimental setup is shown in Fig. 4. As a source of the Gaussian beam was used the Continuum Minilite II Laser. The sample was moved along the axis of the focused laser beam with the increment of 1 μm. The experimental set-up was operated by LabVIEW program and the data were collected by computer. Fig. 5 shows a closed aperture Z-Scan curve of the titled composites using 5 ns Nd:YAG laser having an energy of 0.75 mJ at 532 nm wavelength. The Gaussian beam spot radius at focus was $w_0 = 18$ μm which corresponded to power density equal to $I_0 = 4.6$ GW/cm^2. The