materials proceedings

MDPI

Proceeding Paper

Exploring Optical Nonlinearities of Glass Nanocomposites Made of Bimetallic Nanoparticles and Mesogenic Metal Alkanoates †

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† Presented at the 4th International Online Conference on Nanomaterials, 5–19 May 2023; Available online: https://iocn2023.sciforum.net.

Abstract: The unique properties of nanomaterials along with their suitability for photonics applications can be explored by dispersing nanodopants in a transparent glass matrix. As a rule, the creation of glass nanocomposites involves a synthesis of nanoparticles followed by their dispersion in a glass host. This laborious two-step process can be simplified if glass-forming liquid crystals are used as a nanoreactor and host matrix. In this paper, we discuss a successful realization of this approach using mesogenic metal alkanoates for the fabrication of unconventional glass nanocomposites containing metal and/or bimetallic nanoparticles. More specifically, metal (gold and silver) and bimetallic (silver-gold) nanoparticles are synthesized in the liquid crystal phase of a glass-forming cadmium octanoate. Upon cooling cadmium octanoate samples containing the synthesized nanoparticles easily vitrify resulting in the formation of glass nanocomposites. The produced glass nanocomposites exhibit a relatively strong (10^{-8}–10^{-7} esu) nonlinear-optical response tested by means of a Z-scan technique and utilizing visible (532 nm) and near-infrared (1064 nm) nanosecond laser pulses. The evaluated values of the effective nonlinear absorption coefficients and nonlinear refractive indices of the studied samples depend on their composition and on the intensity of laser beams thus revealing the presence of several nonlinear-optical mechanisms acting simultaneously. Potential applications of the designed glass nanocomposites are also discussed.

Keywords: nanomaterials; metal nanoparticles; bimetallic nanoparticles: liquid crystal glass; nanocomposites; nonlinear-optical materials

Citation: Rudenko, V.; Tolochko, A.; Bugaychuk, S.; Zhulai, D.; Klimusheva, G.; Yaremchuk, G.; Mirnaya, T.; Garbovskiy, Y. Exploring Optical Nonlinearities of Glass Nanocomposites Made of Bimetallic Nanoparticles and Mesogenic Metal Alkanoates. *Mater. Proc.* **2023**, *14*, x. https://doi.org/10.3390/xxxxx

Published: 5 May 2023

1. Introduction

Game-changing and disruptive technologies depend on the development of advanced optical materials capable of controlling light [1]. Numerous studies of optical and nonlinear-optical properties of metal nanomaterials and nanostructures performed during the last two decades resulted in new and exciting areas of research including plasmonics, metamaterials and metasurfaces, and epsilon-near zero materials, to name a few [2]. As a rule, material characterization of metal nanoparticles synthesized using chemical, physical, or biological methods is performed by properly dispersing them in a host matrix [3]. The most common host matrices are either isotropic liquids [3,4] or inorganic glass [4]. In this conference paper we discuss how to use glass-forming ionic liquid crystals made of metal alkanoates for a template synthesis of metal nanoparticles and to produce unconventional glass nanocomposites (metal alkanoate-based host containing metal and bimetallic nanoparticles) exhibiting a relatively strong (10^{-8}–10^{-7} esu) nonlinear-optical response. We also provide a brief overview of basic nonlinear-optical parameters of such nanocomposites produced and studied by our research team during the 2018–2022 period. In addition, we compare nonlinear-optical performance of the studied samples by comparing their figure of merit (FoM) values.

2. Materials

Metal alkanoates $(C_nH_{2n+1}COO^-)_2{}^{-k/2}\ M^{+k}$, where M^{+k} is a mono- (k = 1), di- (k = 2), or trivalent (k = 3) metal cation) can exhibit a great variety of condensed states of matter including liquids, thermotropic and lyotropic liquid crystals, solid and plastic crystals, Langmuir-Blodgett films, and glass [5,6]. Liquid crystal phases of metal alkanoates can be used for template synthesis of nanomaterials [5,7]. Ionic liquid crystals made of metal alkanoates are excellent glass forming materials. This feature allows for the production of liquid crystal glass containing nanoparticles [5]. Metal (gold and silver) and bimetallic (silver/gold) nanoparticles were synthesized using an ionic liquid crystal phase of cadmium octanoate $C_7H_{15}COO)_2{}^{-1}Cd^{+2}$ (abbreviated CdC8) as described in [8–10]. The concentration of nanoparticles was 4% mol. Glass nanocomposites stable at room temperature were obtained by cooling liquid crystals CdC8 containing synthesized metal nanoparticles. In experiments a sandwich-type cell was utilized (the cell thickness was 20-50 μm). It should be noted that pure (undoped) CdC8 is transparent within a visible spectral range and does not exhibit nonlinear-optical response under similar excitation conditions.

Basic materials parameters of the studied samples are listed in Table 1.

Table 1. Basic parameters of nanocomposites made of smectic glass CdC_8 and metal nanoparticles.

Nanoparticle	Geometry	Optical Properties	Nonlinear-Optical Response	Ref.
Au	Spherical, diameter $d = 14$ nm	The absorption band due to a surface plasmon resonance with a maximum around 550 nm	Both nonlinear absorption and nonlinear refraction effects	[8]
Ag	Spherical, $d = 20$ nm	The absorption band due to a surface plasmon resonance with a maximum around 440 nm	Both nonlinear absorption and nonlinear refraction effects	[8]
Ag/Au	Homogeneous bimetallic alloy, spherical, diameter $d = 12$ nm	The absorption band with a maximum at 525 nm	Both nonlinear absorption and nonlinear refraction effects	[9,10]
Ag/Au	Core/shell structure, Ag/Au core ($d = 26$ nm) and Au shell of thickness 8.5 nm	The absorption band with two maxima (at 440 nm and at 520 nm)	Both nonlinear absorption and nonlinear refraction effects	[9,10]

3. Experimental Methods

Nonlinear-optical characterization of the samples listed in Table 1 was performed using a standard Z-scan technique [2]. A laser beam used in experiments has the following parameters: the pulse duration $\tau = 9$ ns, the wavelength $\lambda = 532$ nm and $\lambda = 1064$ nm, the repetition rate $f = 0.5$ Hz, and the peak intensity $I_0 = 8 - 40$ MW/cm² [8–10].

4. Experimental Results

The produced samples exhibit both nonlinear-refraction and nonlinear absorption [8–10]. Interestingly, the evaluated values of the nonlinear absorption coefficients β and nonlinear refractive indices n_2 depend on intensity of a laser beam I_0 as can be seen from Table 2.

Table 2. Nonlinear-optical parameters of the studied nanocomposites.

Sample	I_0, MW/cm²	λ, nm	n_2, cm²/W	β, cm/W	FoM *	Ref.
CdC8 + Ag	10.45	532	-	-9.17×10^{-5}	-	[8]
	17.69		-3.91×10^{-10}	-7.50×10^{-5}	0.392	
	26.45		-5.03×10^{-10}	-4.74×10^{-5}	0.798	
	37.99		-6.96×10^{-10}	-3.11×10^{-5}	1.683	
CdC8 + Au	10.85		-	-1.29×10^{-5}	-	[8]
	18.23		-3.53×10^{-10}	2.03×10^{-5}	1.308	
	26.01		-2.87×10^{-10}	3.44×10^{-5}	0.627	
	35.32		-4.96×10^{-10}	3.96×10^{-5}	0.942	
CdC8 + Ag/Au (homogeneous alloy)	2.21	1064	-1.13×10^{-9}	1.63×10^{-4}	0.261	[9,10]
	3.79		-6.68×10^{-10}	0.95×10^{-4}	0.264	
	8.76		-2.31×10^{-10}	1.03×10^{-4}	0.084	
	9.44		-1.49×10^{-10}	-	-	
	13.7		-6.77×10^{-11}	-	-	
CdC8 + Ag/Au homogeneous alloy	11	532	-2.39×10^{-10}	3.7×10^{-5}	0.486	[9]
CdC8 + Ag/Au core and Au shell	12.5	532	-3.55×10^{-10}	2.5×10^{-5}	1.068	[9]
CdC8 + Ag/Au core and Au shell	2.29	1064	5.1×10^{-9}	0.35×10^{-4}	5.478	[10]
	3.52		1.88×10^{-9}	0.37×10^{-4}	1.910	
	9.11		6.56×10^{-10}	0.05×10^{-4}	4.93	
	10.58		3.04×10^{-10}	-	-	

* $FoM = \left|\frac{4n_2}{\beta\lambda}\right|$.

According to Table 2, depending on the composition of the studied samples, they can exhibit both positive and negative values of the effective nonlinear absorption coefficients β and nonlinear refractive indices n_2. Moreover, both β and n_2 depend on the intensity of a laser beam. As was discussed in [8–10], the observed intensity dependence of the effective nonlinear absorption coefficients and nonlinear refractive indices is caused by a simultaneous presence of several nonlinear-optical mechanisms including saturable absorption, effective two-photon absorption accounting for both pure two-photon absorption and one photon assisted excited state absorption (reverse saturable absorption), nonlinear-optical scattering, the local field factor effects, intrinsic optical nonlinearities of metal nanoparticles, and thermal nonlinearity due to photo-elastic tensions developed in the glass host [8–10].

The computed values of FoM are also listed in Table 2. Glass nanocomposites containing core-shell nanoparticles are characterized by large values (1–5) of FoM thus suggesting possibility of their use for applications relying on third-order optical nonlinearities (amplitude and phase modulation, optical limiting, and ultrafast optical switching, to name a few).

5. Conclusions

Metal alkanoates (CdC8) are very promising materials to produce nanocomposites made of unconventional smectic glass and metal (Au, Ag) nanoparticles of different types including core-shell structures (Table 1). Such materials exhibit a relatively strong nonlinear-optical response (Table 2) overlapping with or exceeding the reported values [4,11]. The produced materials, especially smectic glass doped with core-shell nanoparticles, are also promising for photonics applications because of large values (1-5) of their FoM (Table 2).

Author Contributions: Conceptualization, G.K., S.B., T.M., and Y.G.; methodology, G.K., S.B., D.Z., T.M., and V. R.; software, A.T.; validation, V. R., A.T., D.Z., and G.Y.; formal analysis, V.R., A.T., S.B., D.Z., G.K., G.Y., T.M., and Y.G.; investigation, V.R., A.T., S.B., D.Z., G.K., G.Y., T.Y., and Y.G.; resources, G.V., T.M., and Y.G.; data curation, G.V., S.B., and Y.G.; writing—original draft preparation, V.R., A.T., S.B., D.Z., G.V., G.Y., and T.M.; writing—review and editing, G.V., S.B., and Y.G.; supervision, G.V.; project administration, G.V., funding acquisition, G.V., S.B., T.M., and Y.G. All authors have read and agreed to the published version of the manuscript.

Funding: This work was performed within the target complex program of basic research of the National Academy of Sciences of Ukraine within the projects 1.4.B/219. 3/20-H, B/197 and N. 16 (6541230). This publication is also connected to a research project funded by the German National Academy of Sciences Leopoldina under a Leopoldina Ukraine Distinguished Fellowship.

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.

Data Availability Statement: All data that support the findings of this study are included within the article.

Acknowledgments: The authors (V.R., A. T., S. B., D. Z., G.K., G.Y., and T.M.) acknowledge the support of the National Academy of Sciences of Ukraine (projects № 1.4.B/219, 3/20-H, B/197, and N. 6 (6541230). S. B. expresses her deep gratitude for financial support of the National Academy of Sciences of Ukraine (grants No 1.4.B/219), Université de Lille France (Laboratoire de Physique des Lasers, Atomes et Mol\'ecules (PhLAM) Faculté des Sciences et Technologies), and Le fonds spécial Solidarité Ukraine du programme PAUSE. Y. G. would like to acknowledge funding from the CCSU AAUP faculty research grant.

Conflicts of Interest: The authors declare no conflict of interest.

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