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Acoustically induced optical effects in Pr^{3+} and Tm^{3+} doped calcium gadolinium oxyborate nanocomposites

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ABSTRACT

Acoustically induced two-photon absorption (AITPA) and optical Kerr effect (AIOKE) in Pr and Tm doped calcium gadolinium oxyborate $Ca_4GdO(BO_3)_3$ (CGOB) nanocrystallites (with sizes below 60 nm) prepared by sol–gel method and embedded into the PMMA matrices were studied. The source of the acoustical field generated the frequency equal to about 1.2 MHz and achieved maximal acoustical power density equal to about 6 W/cm^2. The AITPA was measured at fundamental Er:glass laser wavelength (1.54 μm) and was observed only during applying of the prolonged acoustical field. The AITPA effect was substantially higher for the Tm^{3+} doped composites than for the Pr^{3+} doped ones. With increasing acoustical power, the AITPA increases achieving its maximal value at acoustical power density equal to about 4.70 W/cm^2. Temperature dependences have demonstrated the maximal values of the AITPA at temperatures equal to about 310 K corresponding to the AITPA value equal to about 3.4 cm/GW. At the same time at acoustical power density about 3.8 W/cm^2 the AIOKE achieves its minimum for the Pr doped CGOB nanocomposites. So one can expect that these two effects have different signs of contribution caused by the acoustical field.

1. Introduction

The investigations of acoustically induced nonlinear optical effects, mainly devoted to studies of the optical second harmonic generation, were published in several works [1–4]. The effects were caused prevailingly by a spatial asymmetry of photo carriers excitation under external acoustical power [4]. Such asymmetry was determined by strong overlap of electron–hole and electron–phonon interactions. Following the very good optical and piezooptical properties of the borate crystals [5] one can expect that such materials may also be promising for the acoustically induced nonlinear optical effects. Owing to excellent acoustical and nonlinear optical properties of the hybrid organic-inorganic nanocomposites one can expect that these materials may be promising for the acoustically induced nonlinear optical effects. Particular interest may cause nanocrystallites incorporated into the polymer matrices [6,7]. These effects are described by the fourth rank polar tensors, so it may be interesting to study also another optical effects described by this tensor, in particularly acoustically induced optical Kerr effect (AIOKE) and two-photon absorption (AITPA) which are determined by the real and imaginary parts of fourth rank polar tensors. Such effects are called usually as third order optical effects. Following the reasons presented above in the present work we explore the AITPA and AIOKE features of the Tm and Pr doped CGOB NC embedded into the poly(methyl methacrylate) (PMMA) polymer matrices. These materials could be of interest in optically and acoustically operated triggers for laser light.

2. Experimental details

Nanocrystalline (NC) powders of calcium gadolinium oxyborates CGOB doped with thulium or praseodymium ions were synthesized by means of sol–gel method. Firstly, gadolinium oxide was dissolved in acetic acid during 8 h at 65 °C. Thulium and praseodymium oxides were dissolved in nitric acid and then these solutions were evaporated. Next, such obtained thulium or praseodymium nitrates were dissolved in de-ionized water and added to gadolinium acetate solution. Boron oxides and calcium carbonates were dissolved in hot water and acetic acid, respectively. The stoichiometric amounts of all solutions were mixed during 2 h at 65 °C. Finally, the complexing agent 1,2-ethanediol was added and the sol was stirred for next 2 h. After concentrating this sol solution by slow evaporation, the gel was dried at 120 °C during 12 h. Then the gel was ground to powder and calcined in alundum crucible from room temperature to 1000 °C at a rate of 5 °C/min and kept at the elevated temperature during 12 h. All processes were performed under air atmosphere.

In this study, samples containing 0.5% and 1% of the rare earth's ions in weighting units of active substance were prepared. An appropriate amount of optically active substances in form of powder was placed in a solution of poly(methyl methacry-

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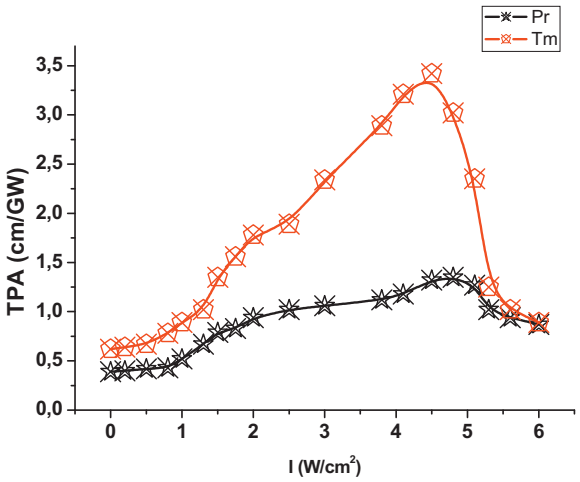

Fig. 1. Acoustically induced dependences of the two-photon absorption in the Pr and Tm doped nanocomposites at temperature about 310 K.

late) (PMMA) in dichloromethane. The nanopowders were additionally crushed by focused acoustical field and filtered by osmotic filters to achieve the sizes of the NC below 60 nm. The resultant dispersion was mixed and evaporated to remove the excess of solvent. When the solution was very viscous, but still liquid, it was poured into a circular form 1 cm in diameter. High viscosity ensured that no significant sedimentation took place. The samples were dried at room temperature for three days, then removed from the form and polished. The thickness of the samples was up to 1 cm.

The AITPA measurements were done using the Er:glass 20 ns laser with 10 Hz frequency repetition. The evaluations of the AITPA coefficients were done following the nonlinear absorption measurements.

The detection was performed by fast response photomultiplier. The acoustical field was applied using $LiNbO_3$ piezoelectric acoustical transducers (AT) which allowed to obtain the acoustical frequencies equal to about 1.2 MHz. The transducers were attached to the nanocomposites by cyathim glue. The set-up allowed to transfer up to 37% of the acoustical power to the nanocomposites

For registration of the changes of refractive indices due to the AIOKE we used doubled polarimeter which registered the changes of the birefringence under the pulses of nanosecond duration. To detect the nonlinear refractive indices we used one mode 20 mW He–Ne laser at wavelength 633.3 nm and a polarimeter which allowed to fix the changes of the birefringence with precision up to 10^{-6} which in turn gave an opportunity to achieve the peak power pulses with power density equal to about 1 GW/cm^2 to detect the changes of the AIOKE coefficients with precision up to the 10^{-23} m^2/W. The AITPA coefficients were evaluated following the nonlinear absorption with precision up to 0.2 cm/GW.

We have performed the measurements for the rare earth's doped nanocomposite samples possessing the content of the NC equal to about 0.5, 1, 2, 3, 4.2, 4.7, 5.3, and 6.1% in weighting units. The further enhancement of the NC content favored formation of aggregated states.

3. Results and discussions

In Fig. 1 the dependences of the AITPA versus the applied acoustical power densities are presented. The results are presented only for the optimal conditions, which in our case corresponded to the NC content of about 4.7% of nanoparticles containing 0.5% and 1% of the rare earth's ions. 1% samples demonstrated substantially weaker effects. The presented figure clearly shows that the increasing acoustical power favors the occurrence of the AITPA, which achieves its maximum value at acoustical power density equal to about 4.7 W/cm^2. It is principal that for the Tm^{3+} doped nanocomposites the effect is at least three times stronger than for the Pr^{3+}-doped nanocomposites. After further enhancement of the applied acoustical wave power density the effect is strongly suppressed. This fact may indicate on the occurrence of the multiphonon acoustical waves, which destroy the acoustically induced states through the electrostriction and piezoelectric contribution.

Maximal output of acoustically stimulated nonlinear optical responses were achieved for parallel directions of the acoustical wave displacement and polarization of the incident fundamental laser beam propagating perpendicularly to the polarization of the superimposed acoustical field. We found that deviations from such parallelism up to 5° leads to at least 25% suppression of the effect.

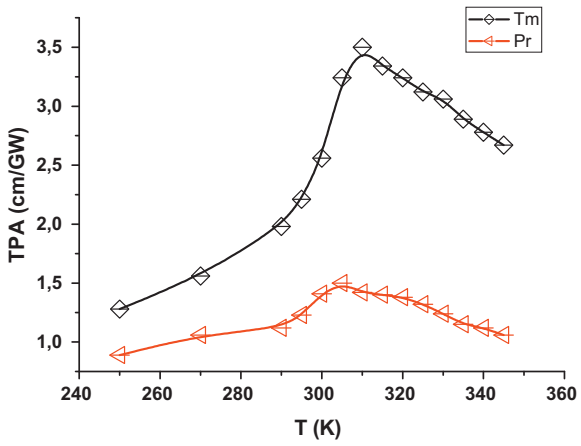

Fig. 2. Temperature dependence of the AITPA coefficients for two different composites at acoustical power density equal to about 3.8 W/cm^2.

Fig. 2 shows principal temperature dependences for the AITPA which show that at about 310 K the effect is maximal. So one can expect that the temperature here plays important role in the acoustically induced dipole moments occurring on the border between the nanocrystallites and the surrounding polymer matrices. Simultaneously the further increase of the temperature may disorder such induced effects and we observe the occurrence of the maxima in the corresponding dependences reflecting the competition between the induced ordering and temperature disorder.

The acoustically induced dependence for the AIOKE is principally different (see Fig. 3). We clearly see a huge minimum for the acoustical power densities equal to about 3.8 W/cm^2. And the observed changes are independent on temperature contrary to the AITPA effect.

Such principal differences in the acoustically stimulated behaviors of the AIOKE and AITPA may reflect the fact that the imaginary part of the third order nonlinear optical effect is different with respect to the real one. Because the effects are caused by electrostriction and piezoelectric phenomena the latter are substantially dependent on the phonon subsystems. So one can expect that these two effects have different influence due to different contribution of the phonon subsystems. In the case of the AIOKE role of the phonon subsystem is more prominent. As a consequence we

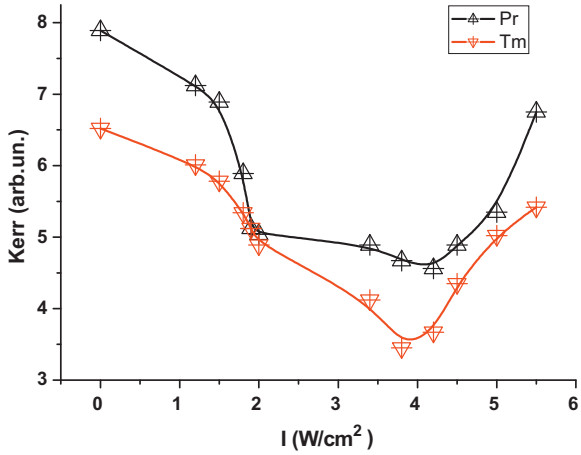

Fig. 3. AIOKE dependences at temperature about 310 K.

observe the corresponding changes. At the same time the changes for the AIOKE are higher for the Pr doped compounds.

The presented dependences may confirm a principal role of electron-acoustical-phonon interactions of higher orders [8].

The presented experimental data, particularly the non-linear acoustical dependences as well as sensitivity to temperature may indicate that origin of the observed phenomenon is caused by acoustically induced phonons, effectively interacting with the electron sub-systems. The phenomenology of interaction has piezoelectric-electrostricted origin and favors charge density redistribution similarly to the second harmonic generation observed under influence of electron beam [9].

Concerning the electrostriction contributions, we should emphasize that effective contribution to the second-order susceptibilities gives only non-centrosymmetric modes, hence, in this case we observe the effects in centrosymmetric media.

The observed finding show that the AIOTPA and AIOKE showing different acoustically dependent behavior may serve as promising tools for the design of the acoustically operated quantum electronic devices.

4. Conclusions

In the present work, the acoustically induced OKE and TPA were observed in the Pr and Tm doped calcium gadolinium oxyborate (CGOB) nanocompostes.

We have established the optimal conditions to induce the maximal induced third-order nonlinear optical effects, which in our case corresponded to the NC content equal to about 4.7% by weight of nanoparticles containing 0.5 at.% of the rare earth's ions. It was shown that increasing acoustical power favors the occurrence of the TPA, which achieves its maximum value at acoustical power equal to about 4.8 W/cm^2 at temperature about 310 K. It is principal that for the Tm^{3+} doped nanocomposites the effect is at least three times stronger than for the Pr^{3+} doped nanocomposites. After further enhancement of the applied acoustical wave power density the effect is strongly suppressed. This fact may indicate on the occurrence of the multi-phonon (anharmonic) acoustical waves, which destroy the acoustically induced states through the electrostriction effect. The dependence of the AIOKE versus the acoustical field is quite different and temperature independent. The maximal minimum is observed at the acoustical power densities equal to about 3.8 W/cm^2. Such behaviors may indicate on the different contributions of the electron and phonon subsystems into the effects.

Acknowledgment

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