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Laser operated borate polymer nanocomposites

A.H. Reshak[a,b], G. Lakshminarayana[c,*], Ya.V. Burak[d], V.T. Adamiv[d]

[a] Institute of Physical Biology-South Bohemia University, Nove Hrady 37333, Czech Republic
[b] School of Microelectronic Engineering, University Malaysia Perlis (UniMAP), Block A, Kompleks Pusat Pengajian, 02600 Arau Jejawi, Perlis, Malaysia
[c] Chair of Glass and Ceramics, Department of Materials Science – WW3, University of Erlangen-Nuremberg, Erlangen 91058, Germany
[d] Institute of Physical Optics, Dragomanowa 19, Lviv, Ukraine

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ABSTRACT

We have found that UV polarized treatment of the nanocrystals (non-centrosymmetric $Li_2B_4O_7$ and centrosymmetric α-BaB_2O_4) embedded into the olygoether acrylate photopolymer samples cause substantially different response depending on the laser features. For the $Li_2B_4O_7$ NC, during treatment by pulsed 7 ns laser polarized nitrogen laser pulses at 337 nm we observed substantial red spectral shift of the energy gap from 7.3 eV up to 6.3 eV. The spectral shift is disappeared during the 15 min after the interruption of optical treatment. The effect exists only in the nanocrystallites with sizes below 200 nm. At the same time for the centrosymmetrical α-BaB_2O_4 nanocrystallites this effect was absent. However the photoinduced second order optical effects induced by coherent bicolor treatment by wavelengths 532 nm and 266 nm are enhanced for the α-BaB_2O_4 NC and are absent for the $Li_2B_4O_7$ ones.

1. Introduction

Recently, the inorganic nanocrystallites (NC) embedded into the polymer matrices have gained an increasing interest for their different optoelectronic applications [1]. They possess different properties which originate from interfaces between the polymer matrices and incorporated nanocrystallites. The wide gap crystals and the corresponding NC like borates are of special interest due to the promising optoelectronic properties. Particular interest presents on the wide energy gap non-centrosymmetrical lithium tetraborate (LTB) $Li_2B_4O_7$ crystals [2]. To be appropriate the polymer matrix should have the close values of the refractive indices to avoid any light scattering. So we have chosen the oligoetheracryalte photopolymer matrix [3]. The titled photopolymer matrices possess besides the good optical fitness very good photothermal optical properties and are stable with respect to the external laser light. For comparison we study also the centrosymemtrical α-BaB_2O_4 single crystals.

It is well known that the semi conducting NC with the sizes below 70 nm show substantial changes of the band energy dispersion [4] and corresponding effective energy gaps. This is caused by the reconstructed surface states, which are very sensitive to the surrounding polymer matrices due to enhanced values of the ground state dipole moments for the non-centrosymmetry nanocrystallites. So one can expect that UV-induced polarized light below the energy gap may cause additional photo-occupation of the localized trapping levels and as a consequence it may be a possibility to perform the UV-spectral shift of the effective energy gap in such kinds of NC. At the same time principal role begin to play the crystallite non-centrosymmetry forming additional charged defect states. For comparison we have used the centrosymmetrical α-BaB_2O_4 single nanocrystallites. Complimentary information may be obtained form the studies of the second order susceptibilities.

In the present work we explore influence of the polarized UV-pulsed power density, temperature and NC sizes of the polymer nanocomposites and temperature on the possible shift of the effective energy gap.

2. Sample preparation

Lithium tetraborate ($Li_2B_4O_7$) crystals belong to the space group $I4_1cd$ (point group 4 mm) [5]. The technology of $Li_2B_4O_7$ synthesis is very sensitive to the initial chemicals. The experience of the works with borates had shown that the mostly advantageous for $Li_2B_4O_7$ synthesis from the technological point of view are lithium carbonate (Li_2CO_3) and boric acid (H_3BO_3) of high purity, which during the heating process decompose just into the suitable oxides. As a result, the method for multi-graded and multi-staged synthesis of $Li_2B_4O_7$ was successfully elaborated and used. All this process can be described in a form of equation for the chemical reaction:

$$Li_2CO_3 + 4H_3BO_3 \rightarrow Li_2B_4O_7 + CO_2\uparrow + 6H_2O\uparrow$$

Compound of $Li_2B_4O_7$ was melted congruently and the classical Czochralski method was applied for the growth of its single

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[*] Corresponding author. Tel.: +49 9131 85 27564.
E-mail address: glnphysics@rediffmail.com (G. Lakshminarayana).

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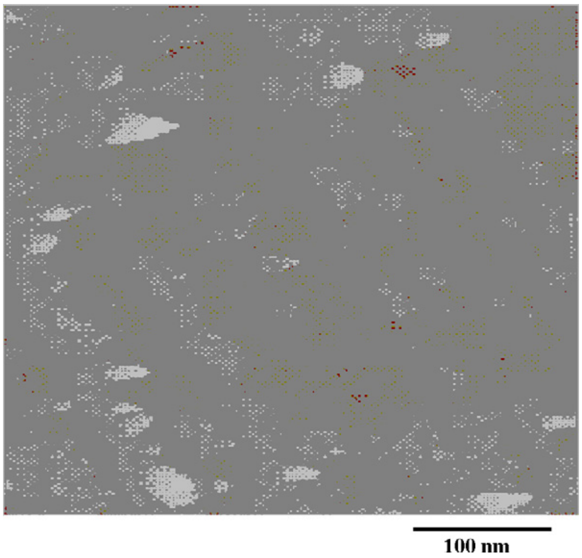

Fig. 1. TEM picture of the titled nanocomposites.

crystals. The most optimal growth parameters, ascertained experimentally, were: the axis of growth [0 0 1], seed pulling velocity 0.3 mm/h, its rotation velocity not more than 10 rpm. By this method $Li_2B_4O_7$ single crystals of high optical quality with sizes Ø (20–25) mm × (20–40) mm were obtained [6].

Barium borate (BaB_2O_4) exists in two different symmetry crystal modifications of trigonal system: high-temperature α-BaB_2O_4 and low-temperature β-BaB_2O_4 with space groups of symmetry R$\bar{3}$c (D_{3d}^6) (point group $\bar{3}m$) and R3c (C_{3v}^6) (point group 3m) [7], respectively. The phase transition β → α takes place at 1198 K, but both modifications are stable at room temperature. The pseudo-layered structure, in which Ba^{2+} ions alternate with almost planar isolated borate rings $(B_3O_6)^{3-}$, is typical for both modifications of BaB_2O_4 crystals. The difference in symmetry between α-BaB_2O_4 and β-BaB_2O_4 are caused by a difference in the positions of Ba^{2+} ions in the lattice: centrosymmetrical for α- and noncentric for β-modification. Such structural differences cause considerable differences of physical properties for these compounds. For example, effective nonlinear optical characteristics connected with charge transfer from oxygen to boron in metaborate's anion $(B_3O_6)^{3-}$, have been discovered in β-BaB_2O_4 crystals, and this is absent in α-BaB_2O_4.

For the synthesis of growth mixture α-BaB_2O_4 the barium carbonate ($BaCO_3$) and boric acid (H_3BO_3) of high purity, chemical agents were used. The process of the synthesis can be described in a form of equation for the chemical reaction:

$$BaCO_3 + 2H_3BO_3 \rightarrow BaB_2O_4 + 3H_2O + CO_2.$$

α-BaB_2O_4 single crystals were grown from stoichiometric melt at 1368 K by direct Czochralsky method in Pt-crucible in air atmosphere [8]. The most optimal growth parameters, ascertained experimentally, were: the axis of growth [0 0 1], seed pulling velocity 0.5 mm/h, its rotation velocity not more than 20 rpm. The grown crystals Ø 25 mm × 10–15 mm possessed high optical homogeneity.

The NC was milled using acoustical field and was incorporated into the photopolymer olygoether acrylate matrices as described in the Ref. [10]. We have prepared the samples with the content of the NC equal to about 0.5%, 1.0%, 2%, 3%, 4%, and 5%, in weighting units. The control of their TEM structure was done by JEOL-100. From Fig. 1 one can see that the NC is incorporated into the polymer matrices and the evaluation of the size dispersion was equal to about 12 nm.

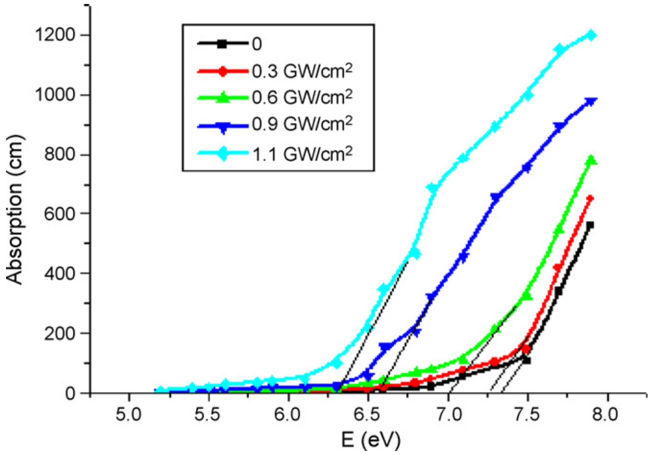

Fig. 2. UV-induced spectral shift of energy gap under influence of the UV-induced laser light.

The treatment is performed by the 337 nm, 7 ns UV pulse laser with the variations of the laser power densities up to 1 GW/cm^2. The U-7000 Automated Vacuum UV System was used as vacuum spectrophotometer with resolution about 7 nm. The laser beam was focused by MgF_2 windows on the samples with the diameters about 1 mm. The probing beam form the UV source also was incident on the samples which were diagrammed. The UV-induced laser pulses possessed the frequency repetition about 10 Hz and the beam of the pumping laser and of the probing spectrophotometer were overlapped.

3. Results and discussion

In Fig. 2 are presented the UV-absorption edges for the titled nanocompsites under influence of the pulsed UV-laser irradiation of different powers. One can clearly see that the absorption edge is shifted from 7.3 eV up to 6.31 eV at 1.1 GW/cm^2 laser irradiation.

The absorption is shown after the saturation during the 3–4 min. All the measurements were done at T = 77 K. This fact may indicate the principal role for electron–phonon interactions participating in the absorption edge. The lowering of temperature stimulates the substantial changes in trapping of the photo-excited electrons. As a consequence the optically induced electron–phonon anharmonicities forming the internal effective electric field may play substantial role in the effect observed.

It is principal that the observed spectral shift is very sensitive to the temperature and exists only at low temperatures (see Fig. 3). Another principal factor here is a content dependence of the energy gap versus the content of the NC (Fig. 4). One can see that the maximal energy gap exists at 3% of TBL nanocrystallites in weighting units. Such dependence may indicate on a principal role played by the NC interfaces which possess a fixed effective nanointerface which contribute to the effects observed. As a consequence such effects may be very crucial for the observed UV-induced energy gap shift. It is necessary to underline that the effect exists only during the photo-treatment and disappears several minutes after interruption of the UV-laser treatment. Moreover the effect is absolutely absent for the crystallites with sizes about 200 nm. So it is not observed for the bulk crystals.

This phenomenon may be of interest for the UV-optical trigger because it allows operating by the UV-absorption transparency, which is principal for the UV-optoelectronic.

For comparison we have performed the studies of the UV-induced shift for the centrosymmetric crystals of α-BaB_2O_4. We have found that the changes of the photoinduced absorption does not exceed 1.4 cm^{-1}.

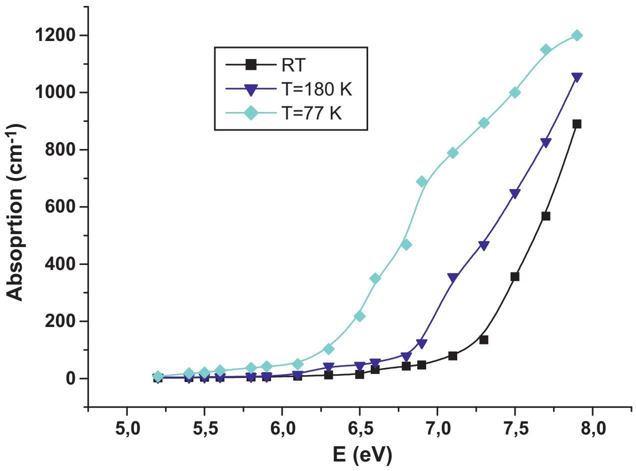

Fig. 3. The absorption edge measured at different temperatures.

This fact may reflect a principal role of the non-centrosymmetry in the observed dependences. The higher non-centrosymemtry favors additional shift of the absorption edge due to the photoinduced polarization. At the same time this fact may indicate that the $Li_2B_4O_7$ nanocrystallites do not have a possibility to form additional non-centrosymmetry. From another side the centrosymemtrical α-BaB_2O_4 NC may form additional potential for the formation of non-centrosymmetry.

To check this conception we have performed additional optical poling of the nanocomposites of the both crystals by a method similar to the described in the reference [9]. The fundamental laser we have used was pulsed doubled frequency 10 ns Nd: YAG lasers with powers varying up to 1.2 GW/cm^2. The writing doubled frequency beam at 266 nm had power density from 8 to 5 times less. The optical treatment was performed during the 4–5 min and control of the photoinduced grating was performed by measuring of the grating diffracted laser beam. The polarization of the photoinduced beam was s-p and during the measurements of the SHG the doubled frequency (writing beam) was switched off.

Following the presented results (see Fig. 5) one can clearly see that the $Li_2B_4O_7$ nanocrystallites are almost non-sensitive to the photo-inducing power densities. At the same time the α-BaB_2O_4 NC demonstrate clear increase. One can conclude that the role of the polarized trapping states may play here a crucial role [10]. Additional role may also play the charged defect states [11]. Such materials may also be promising during preparation of the Mn doped $Li_2B_4O_7$ nanocrystallites [12].

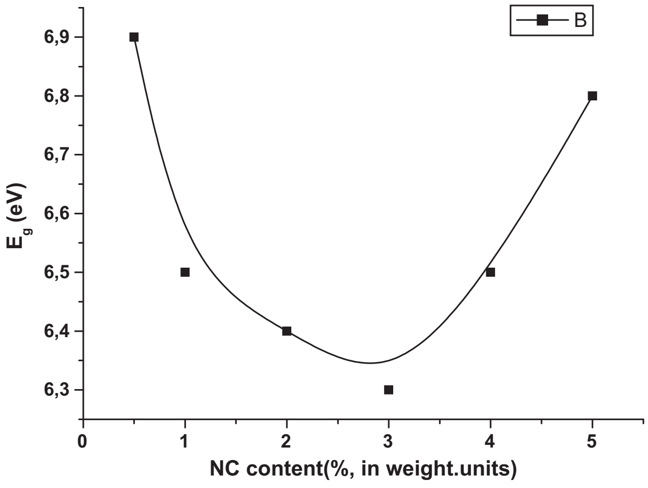

Fig. 4. Dependence of effective energy gap at different NP content.

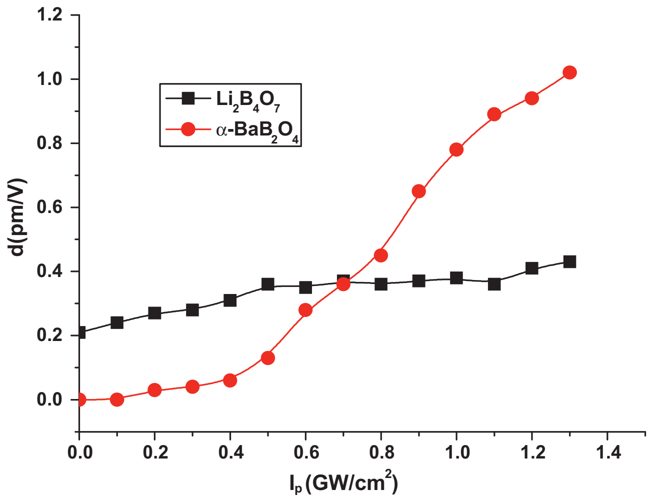

Fig. 5. Dependence of the second order susceptibility for the 532 nm during the optical treatment of the borate nanocomposites by 532 nm and 266 nm coherent laser beams versus the fundamental laser wavelength.

The performed studies indicate that one of the possible ways to enhance their photoinduced susceptibilities consists in the appropriate changes of the polymer matrices due to variation of their polarizabilities, which will be a subject of a separate work in future.

4. Conclusions

We have studied different influence of the laser treatment on the behaviors of the optical effects in the $Li_2B_4O_7$ and α-BaB_2O_4 nanocrystallites on the illumination by laser beams with different features. UV polarized treatment of the $Li_2B_4O_7$ NC (TBL NC) embedded into the olygoether acrylte photopolymer films with the pulsed 7 ns laser polarized nitrogen laser pulses at 337 nm causes substantial red spectral shift of the energy gap from 7.3 eV up to 6.31 eV at 1.1 GW/cm^2 UV-laser irradiation at $T = 77$ K. With the increasing temperature and the lower UV-induced laser power densities the effect is decreased. The optically induced electron–phonon anharmonicities forming the internal effective electric field may play substantial role in the effect observed exists at 3% of TBL nanocrystallites in weighting units. Such dependence may indicate a principal role played by the NC interfaces which possess a fixed effective nanointerface which contribute to the effects observed. As a consequence such effects may be very crucial for the observed UV-induced energy gap shift. It is necessary to underline that the effect exists only during the photo-treatment and disappears several minutes after interruption of the UV-laser treatment. Moreover the effect is absolutely absent for the crystallites with sizes about 200 nm. So it is not observed for the bulk crystals. At the same time the centrosymmetrical α-BaB_2O_4 NC at the same treatment conditions do not show significant changes.

Acknowledgments

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