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Electrooptics parameters of the BiBO:Tm^{3+} glass nanoparticles embedded in polymer matrices

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Abstract We have found that BiB_3O_6:Tm^{3+} glass nanoparticles (NP) incorporated into the polymethylmethacrylate (PMMA) and polycarbonate (PC) polymer matrices additionally treated by dc-electric field (at electric strength about 8 kV/cm) at temperatures above the glassing temperature of the polymers show promising values of electrooptics coefficients (up to 10 pm/V at $\lambda = 633$ nm). It was established that only during incorporation into the highly polarized PC matrices one could observe an enhancement of the electroopitcs effect (EOE) coefficient with increasing time of the dc-electric treatment. The main increase was observed for all the samples at times higher than 80 min of dc-electric field treatment at temperature above the glassing temperatures of the corresponding polymers. The most striking feature is the achievement of effective electrooptics coefficient value below than 10 pm/V ($\lambda = 633$ nm) for the 4% content of the Tm doped BiBO glass nanoparticle (NP) embedded in the PC matrix. In the case of the bulk glasses the thermal poling unambiguously shows that the achieved maximal values of the electrooptics coefficient did not exceed 3.2 pm/V for 0.5% Tm^{+3} concentration.

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1 Introduction

The borate crystals cause recently enhanced interest due to their excellent nonlinear optical properties, first of all the optical second harmonic generation (SHG) [1–5]. Among the borates particular interest present BiB_3O_6 (BIBO) single crystals which have highly efficient nonlinear optical properties in particularly the second harmonic generation (SHG) [6] as well as in the third harmonic generation (THG) [7] applications. BIBO crystals belong to the non-centrosymmetric monoclinic space group C_2 and their effective second-order susceptibilities are larger than for other nonlinear optical crystals, such as β-BaB_2O_4 and LiB_3O_5. However, it is well known that all the crystals possess a natural limit, which cannot be improved by any technological treatment [8]. In Ref. [9] it was shown that one of promising effects that can be used to enhance the nonlinear susceptibilities consists in the use of partially crystallized non-centrosymmetric compounds and simultaneous application of the photoinducing UV-treatment [10].

It is interesting that up today there were not electrooptical effect (EOE) studies of these materials because in the single crystals this effect is vanishingly small. One can expect that one of promising way may be related to the use of a large number of trapping levels originating from the partial disorder to enhance the EOE efficiency. Additionally due to effective interaction with the anharmonic phonon subsystems, such kinds of physical mechanisms may be crucial for enhancement of linear EOE described by the third rank polar tensors. In the case of BIBO disordered materials a promising tool may be additional formation of the local trapping levels due to doping. Among the possible impurities the rare earth ions are of special interest. However, to form the macroscopic non-centrosymmetry it is necessary to perform additional macroscopic alignment of the crystallites using external dc-electric field. In the present work we apply external dc-electric field which is necessary for formation of macroscopical non-centrosymmetry in BiBO NP incorporated into the polymer matrices of different polarizabilities at temperatures higher than glassing temperature. During such dc-thermal poling the corresponding nanocommposites change their symmetry and manifests the properties similar to the non-centrosymmetric described by polar third-rank tensors may be allowed by symmetry in such media.

In the present work we investigate the dc-electric field induced EOE in the BIBO-Tm^{+3} glasses and corresponding glass NP were incorporated into the polymer matrices. Two types of polymer matrices—low polarizable polymethylmethacrylate (PMMA) and highly polarizable polycarbonate (PC) were chosen for incorporation of NP of the BIBO-Tm^{3+} glasses. We studied the BIBO NP with different content of the Tm^{3+} ions and different content of the NP in the polymer matrices. The comparison with the EOE changes for the bulk BIBO glasses (pure and doped by Tm) is presented. In Sect. 2 the technological aspects of the glass synthesis, formation of NP and incorporation them into the polymer matrices are presented. Section 3 presents the principal results for the EOE coefficients for the BIBO:Tm glass NP incorporated into the polymer matrices.

2 Experimental methodology

Molten borates having high molar content of boric oxide (B_2O_3), like BiBO or CLBO ($CsLiB_6O_{10}$), possess very large viscosity, approaching 10^3 Poise near their crystallization temperature [11]. This feature of many borate melts makes the crystallization of good quality single crystals a difficult task.

The starting melt for BiBO:Tm^{3+} glass fabrication was synthesized from stoichiometric amounts of B_2O_3 (Merck Suprapur), Bi_2O_3 99.999% Aldrich and Tm_2O_3 99.999% Aldrich in a platinum crucible. Thulium ions substituted bismuth ions. To obtain material with known composition, the boron oxide was molten first to remove water, which is easily absorbed by this compound. After finding the mass of molten B_2O_3, appropriate amounts of Bi_2O_3 and Tm_2O_3 were added to the crucible in next step. The melt was stirred with the use of a platinum stirrer at 850 °C for several hours until it became totally transparent. BiBO:Tm glass was produced by pouring the melt onto Pt/Au5% mould and its rapid cooling to temperatures below 400 °C.

The synthesized bulk glasses were mechanically crushed with additional acoustical field treatment. The typical size distribution of the investigated glassy NP following TEM monitoring is shown in Table 1.

The as-obtained glass NP were incorporated into different polymer matrices by spin coating method with the different NP concentration varying from 2% up to 6%. The obtained nanocomposite films were deposited on the glass substrate and their thickness was about 5 μm. The higher content of the NP is limited by formation of the aggregates, which destroy the desirable effects. Afterwards the films were heated up to temperatures about the glassing temperature (about 120 C and 150 C for PMMA and PC, respectively), which correspond to the temperature above the glassing transformations. During this process the measurements of the linear EOE coefficients were performed.

All the measurements were performed for the wavelength 633 nm of the cw 10 mW He–Ne laser. Diameter of the laser beam was about 2 mm. We have found that maximal effective EOE coefficient was achieved for diagonal position of the samples, which corresponded to 45° between the direction of the incident laser field polarization and the applied dc-electric field. The measurements were performed using AC dynamics Senarmont

Table 1 Size distribution of the BIBO:Tm^{3+} glass NP after mechanical and acoustical crushing

Glass NP sizes (nm)	Probability of occurrence
80	25
82	29
105	36
121	46
142	66
160	76
179	24

Size distribution of the BIBO:Tm^{3+} glass NP after mechanical and acoustical crushing. Maximum is observed for the 160 nm glassing NP. We deal with the so-called large-sized nanocrystallites [7], at which the principal effects determining the electropotics coefficients are occurred on the surfaces of the NP

method described in Ref. [12]. General determination of the birefringence induced by low frequency ac field was done by Senarmont method described in the Ref. [13] with birefringence precision up to 10^{-6}. This method has phase shifting plate $\lambda/4$ situated in diagonal position (i.e., 45° with respect to crossed polarizer and analyzer directions). The sinusoidal ac electric field had a frequency of about 1 kHz with maximal amplitude of up to 25 V. On varying the amplitude of the ac voltage, we measured the voltage corresponding to the doubling of the modulated frequency by a lock-in amplifier. The method allows to us to determine the birefringence with a precision equal to about 3×10^{-6}.

3 Results and discussion

The principal results of the measurements of the effective EOE coefficients are presented in Fig. 1. It was found that only during incorporation into the highly polarized PC matrices one could observe an enhancement of the EOE coefficient with the increasing time of dc-field thermal treatment. The main increase is observed for all the samples at times higher than 80 min at temperature above the glassing temperatures of the corresponding polymers. The values of the applied dc-field was equal about 8 kV/cm. The most striking feature is the achievement of effective EOE coefficient value higher than 10 pm/V at $\lambda = 633$ nm for the 4% content of the Tm doped BiBO glass NP incorporated into the PC matrix.

In the case of the bulk glasses (see Fig. 2) the thermal poling performed at 50 C degree below the melting temperature and dc-electric field 10 kV/cm unambiguously show that the achieved maximal values of the EOE

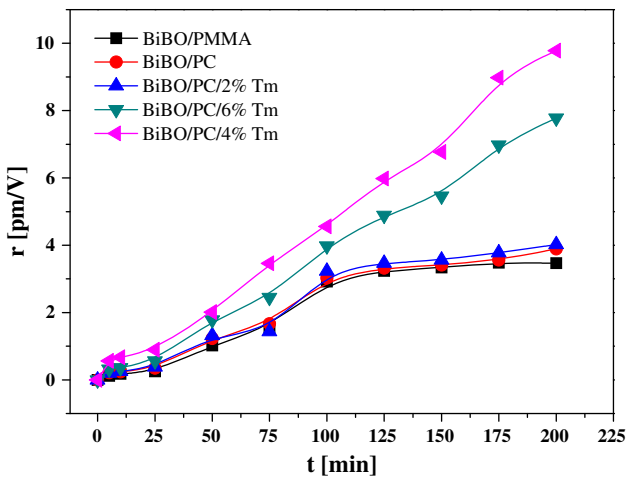

Fig. 1 Dependences of the effective electrooptics coefficient versus the time of dc-electric treatment ($E = 8$ kV/cm) at temperature higher then glassing

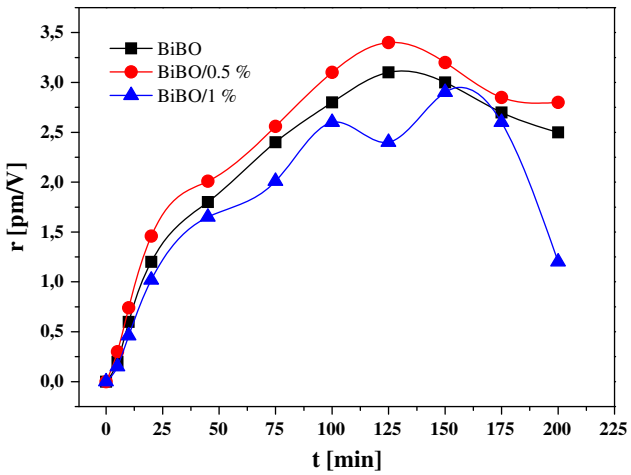

Fig. 2 Dependence of the dc-induced EOE coefficients for the bulk BIBO glasses (pure and doped by 0.5 and 1% of Tm) at 650 °C at applied dc-electric field 10 kV/cm

coefficient did not exceed 3.2 pm/V for 0.5% Tm concentration. This fact confirms a principal role of the NP in the observed dependences and a crucial role of the rare earth doping. Moreover one can see a saturation of the EOE coefficients and even severe decrease for the bulk glasses. The more striking fact is an achievement of the maximal EOE coefficients for the 4% content of the NP. At the 6% there is a decrease up to 12%. For the case of the PMMA matrices the changes are substantially less. The same situation is for the pure bulk glass BIBO and low-doped Tm BIBO glasses. The effect was maximal for the low concentration of the Tm (about 0.5%). In the case of the bulk glasses (treated at dc-electric field and at temperatures below the melting point) the dependences of the EOE unambiguously show that the maximal values of the EOE coefficients did not exceed 3 pm/V for the case of

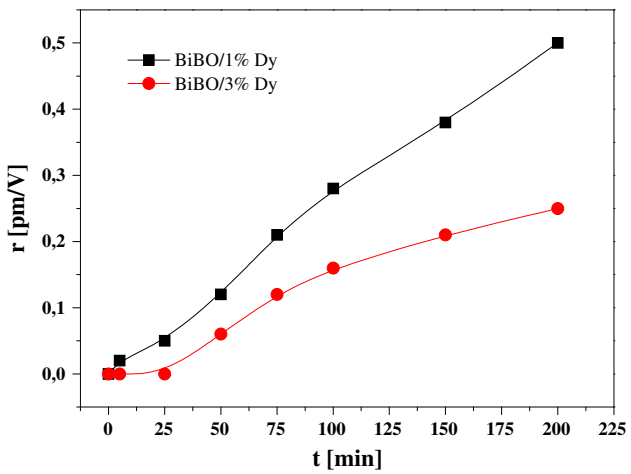

Fig. 3 Dependence of the effective EOE coefficient for the BIBO:Dy^{3+} bulk glasses at temperature about 650 °C

0.5% Tm glasses. However, in this case one can clearly see the existence of the clear maximum (see Fig. 2). The further increase of the time of dc-treatment lead to the drastic decrease of the EOE .

To show the principal role of the Tm rare earth ions we present the same dependences for the Dy^{3+} doped BIBO bulk glasses (Fig. 3). One can see substantially smaller values of the effective EOE coefficients than for the Tm^{3+} doped BiBO glasses. This fact confirms a principal role of the rare ions in the observed electrooptics dependences.

4 Conclusions

It was found that only during incorporation of the BIBI:Tm^{3+} glass NP into the highly polarized PC matrices one can observe an enhancement of the effective EOE coefficients with increasing time of dc-electric field treatment. The main increase is observed for all the samples at dc-electric field treatment times higher than 80 min for temperature above glassing temperatures of the corresponding polymers. The values of the applied dc-field was equal to about 8 kV/cm. The most striking feature is the achievement of effective EOE coefficient value smaller than 10 pm/V ($\lambda = 633$ nm) for the 4% content of the Tm doped BiBO glass nanoparticle (NP) in the PC matrix. In the case of the bulk glasses the thermal poling unambiguously show that the achieved maximal values of the EOE coefficient did not exceed 3.2 pm/V for 0.5% Tm concentration.

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