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Electro-optical properties of $Bi_xLa_ySc_z(BO_3)_4$ ($x+y+z=4$) nanocrystallites having huntite structure incorporated into polymer matrices

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ABSTRACT

Experimental measurements of linear electro-optical coefficients are reported for $Bi_xLa_ySc_z(BO_3)_4$ ($x+y+z=4$) (BLSB) nanocrystallites incorporated into polymer matrices of different polarizabilities. The nanochromophores in the matrices were oriented by external dc-electric field during spin coating. The measurements were performed under illumination of CW semiconducting GaAlAs laser emitting at 1040 nm. We have achieved the maximal values of the Pockels coefficients equal to 3.5 pm/V for the BLSB nanocrystallites incorporated into the polycarbonate matrices. The optimal sizes of nanocrystallites were below 20 nm and their content was equal to about 7.5% (in weight. units). We have eliminated a contribution to the Pockels effect due to the piezo-optical coefficients as well as due to other bothering factors. The temperature influence is very low (due to low ionic contribution), and do not exceed 6%, which is related to low contribution of electron–phonon interaction to the Pockels effect. So these alloys may be proposed as promising materials for high power laser electro-optic modulators.

1. Introduction

The use of borate crystallites as nonlinear optical crystals is of great interest due to their excellent nonlinear optical susceptibilities, good phase matching conditions, etc. [1–7]. One of the promising ways to enhance their nonlinear optical susceptibilities is to form the composites containing the corresponding crystallites embedded into polymer matrices [8,9]. Particularly borates possessing the structure of trigonal huntite derivative $YAl_3(BO_3)_4$ are extensively studied recently [10,11]. Although the lanthanum derivative $LaSc_3(BO_3)_4$ (LSB) has been reported to exist in the noncentrosymmetric trigonal phase [12], it crystallizes in monoclinic variants of the huntite structure in the space group $C2/c$ in the most cases of bulk crystal growth [13].

Nevertheless, the monoclinic structure of LSB can be converted to the trigonal form by doping with a smaller lanthanide ions, for example $La_{1-x}Nd_xSc_3(BO3)4$ (NLSB), $Y_xLa_ySc_z(BO_3)_4$ (YLSB), and $Lu_xLa_ySc_z(BO_3)_4$ (LLSB) [13–15].

In the present paper we will show the possibility of use the nanocrystallites prepared from $Bi_xLa_ySc_z(BO_3)_4$ ($x+y+z=4$) crystalline alloys as nanochromophores for electro-optics. We will explore the influence of the three types of polymer matrices: polycarbonates (PC); polymethylmethacrylate (PMMA) and polyvinylcarbazole (PVK) matrices. These matrices possess different polarizabilities. So crucial role will be played by interfaces separating the polymers and nanointerfaces of the corresponding nanochromophores.

2. Crystal growth

Spontaneous crystallization from a flux was used to obtain $Bi_xLa_ySc_z(BO_3)_4$ crystals. The surplus of Bi_2O_3 and B_2O_3 was chosen as a self-flux to avoid contamination of the growing crystals with other ions. The molar ratio of chemicals used in synthesis of starting composition was the same as in Ref. [16] $La_2O_3:Sc_2O_3:Bi_2O_3:B_2O_3 = 1:1.5:13:13$, where authors found area of huntite-type structure crystallization in quasi-ternary phase diagram of $BiBO_3–LaBO_3–ScBO_3$ system. No previous synthesis of the crystallized material was made. All the components were molten directly in a platinum crucible placed in a vertical resistance furnace having long heating zone and good thermal isolation to secure low thermal gradients during crystallization. The furnace temperature was controlled with Eurotherm 906S programmer. The temperature of the crucible was initially raised to 1100 °C and after 12 h it was lowered at a rate of 3 °C/h. When the crystallization was finished the crystals were decanted from the flux at 850 °C and then the furnace was cooled down to room temperature at a rate of 20 °C/h. The spontaneous crystallization resulted in obtaining

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of many tiny $Bi_xLa_ySc_z(BO_3)_4$ crystals. The as-grown crystals were treated with diluted nitric acid to remove the traces of the flux.

3. Nanocomposite preparation

The as-prepared crystallites were additionally mechanically crushed using the external acoustical field. After additional nano-sized filtration additional separation of the nanocrystallites within the sizes 25–250 nm. After that the crystallites were mixed with the corresponding polymers in different weighting units. During the process of polymer solidification the dc-electric field was applied to orient the particular nanochromophore. It was established that at fields higher than 5–6 kV/cm the orientation of the chromophores was maximal. The thickness of the samples was equal to about 1 mm and non-homogeneity of the nanocrystalline incorporated into the polymer matrices did not exceed 7%.

4. Electro-optical measurements

The electro-optical properties were measured using an illumination of 1040 nm GaAlAs CW 10 mW laser. We have found that maximal effective electro-optical 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 method described in Ref. [17].

The spot diameter of the laser beam was equal to about 800 μm. General determination of the birefringence induced by low-frequency ac-field was done by Senarmont method described in Ref. [18] 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 us to determine the birefringence with a precision equal to about 6×10^{-6}. This allows to achieve the precision of the electro-optical coefficients determination about 0.2 pm/V.

5. Results and discussion

It is necessary to emphasize that for the borate crystals the contribution of the phonon sub-system to electro-optics is below 5–7% [19]. Hence we can consider the electronic contribution as dominant. Generally the linear electro-optical coefficient has two contributions. The first one corresponds to the electronic part and the second one corresponds to the phonon contribution. The phonon part is larger for the crystals possessing large ionic contribution. For example charge transfer between cations and anions determining effective Scigetti charges. In the case of the borates role of cations is limited mainly to the stabilization of the structure and their contribution to the hyperpolarizabilities is small. Following the anionic theory main role in the hyperpolarizabilities determining the nonlinear optical coefficients in borates play borate clusters like BO_3, BO_4, and BO_6. That is why the small phonon contribution to the Pockels effect is typical for crystals possessing large covalence part contributing to the nonlinear optical susceptibility. Usually the electro-optics gives a small contribution when the phonon contribution is small. However, when the particular clusters of borates possess different polarizabilities it may lead to occurrence of significant electro-optical effect, both linear as well as quadratic one. However, it requires separate calculations of the dipole moments of particular clusters and consideration of dipole–dipole interactions, which may be a subject of separate work in a future. Moreover, one can expect that here principal role may play not only the ground state dipole moments, however also the transition dipole moments.

The samples were investigated by the applied dc-electric field of different direction of the applied dc-field. We have analyzed the values of the phase inversion. For this reason we have applied the low-frequency modulated electric field (about 1 kHz) and we have found that the changes of the phase give information about the parameters of the Pockels effect. Especially performed investigations have shown that the values of these coefficients is varied not larger than 4.2% in a space which may be an independent confirmation of large reliability of this crystal for further applications. To eliminate the contribution of elastooptical effect we have performed independent investigations of the elastooptical effect and after we extracted the values of the output Pockels effect.

The principal results of our measurements are given in Fig. 1. One can see a drastic enhancement of the electro-optical coefficients during the decrease of average sizes of nanochromophores. Despite the size distribution was non-monodispersive (up to 20 nm), one can clearly see that the values of the electro-optical coefficients drastically increase at lower sizes up to several times. The maximal enhancement occurs for more polarizable PC matrices and the lowest for the less polarizable PMMA matrices. For the case of the intermediate polivinylkarbazolwe (PVK) matrices we have the electro-optical coefficients which do not exceed 2.4 pm/V. So the polarizability of the polymer matrix plays here the decisive role. The main increase occurs at sizes of nanocrystallites below 80 nm. In this case principal role begins to play the nanointerfaces separating the nanocrystallites and the surrounding polymers. One can expect that the main role in the observed phenomenon belongs to dipole–dipole interactions between the interfaces of the nanocrystals and the ground state dipole moments of the matrix polymers. An external dc-electric field favors additional orientation of the crystallites to obtain the macroscopic noncentrosymmetry.

Additionally we have found that the maximal enhancement of the Pockels coefficients was achieved for the concentration of the nanochromophore about 7.5% in weighting units (see Fig. 2). This may indicate on a principal role of the aggregates occurring at the higher nanochromophore concentrations. Generally one can expect that varying the polymer matrices polarization one can tune the electro-optics coefficients in the range from 1.25 pm/V up to 3.5 pm/V. This fact may be used for preparation of the electro-optical composite materials based on the borate alloys.

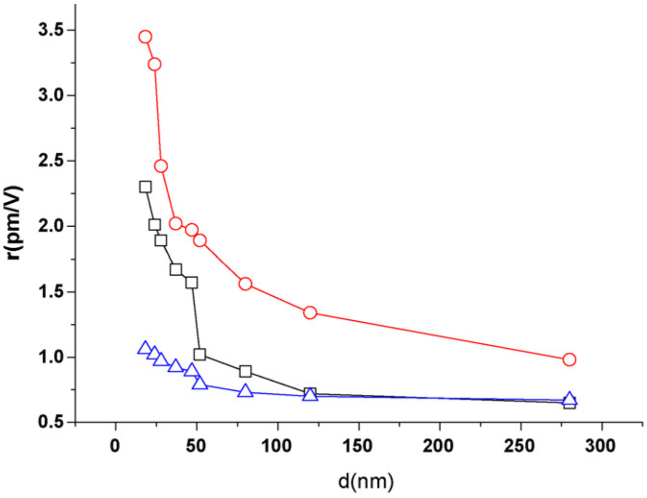

Fig. 1. Size dependence of the effective electro-optical coefficients for different polymer matrices: triangles—PMMA; squares—PVK; rings—PC. All the data are given for the nanoparticle concentration about 7.5% in weighting units.

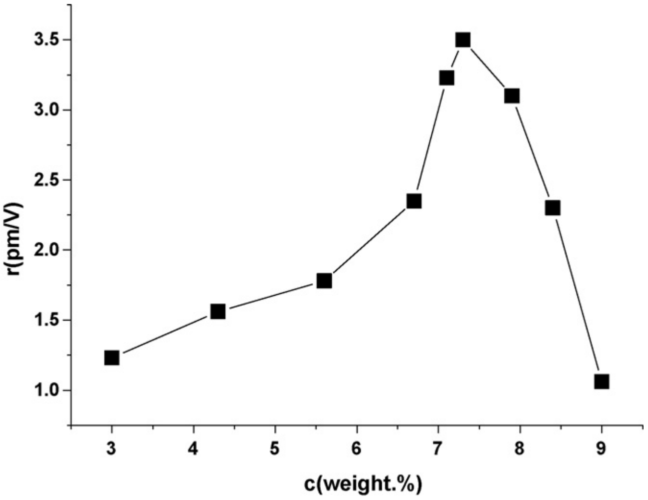

Fig. 2. Typical concentration dependence of the nanocomposites for the PC matrices.

6. Conclusions

Experimental measurements of linear electro-optical coefficients are reported for $Bi_xLa_ySc_z(BO_3)_4$ (BLSB) nanocrystallites incorporated into the polymer matrices of different polarizabilities. The measurements were performed under illumination of CW semiconducting GaAlAs laser emitting at 1040 nm. We have found a drastic enhancement of the electro-optical coefficients during the decrease of average sizes of nanochromophores. Despite the size distribution was non-monodispersive (up to 20 nm), one can clearly see that the values of the electro-optical coefficients drastically increase at lower sizes up to several times. We have achieved the maximal values of the Pockels coefficients equal to 3.5 pm/V for the BLSB nanocrystallites incorporated into the polycarbonate matrices. The optimal sizes of nanocrystallites were below 20 nm and their content was equal to about 7.5% (in weight. units). The maximal enhancement occurs for more polarizable PC matrices and the lowest for the less polarizable PMMA matrices. The main increase occurs at sizes below 80 nm. In this case principal role begins to play the nanointerfaces separating the nanocrystallites and the surrounding polymers. One can expect that the main role in the observed phenomenon belongs to dipole–dipole interactions between the interfaces of the nanocrystals and the ground state dipole moments of the matrix polymers.

Additionally we have found that the maximal enhancement of the Pockels coefficients was achieved for the concentration of the nanochromophore about 7.5% in weighting units.

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