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Absorption, fluorescence and second harmonic generation in Cr^{3+}-doped BiB_3O_6 glasses

W. Kuznik [a,b], I. Fuks-Janczarek [c], A. Wojciechowski [a], I.V. Kityk [a,*], V. Kiisk [d], A. Majchrowski [e], L.R. Jaroszewicz [e], M.G. Brik [f,d], G.U.L. Nagy [g]

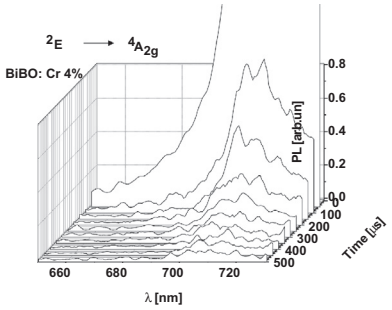
[a] Electrical Engineering Department, Czestochowa University of Technology, Armii Krajowej 17, Czestochowa 42-200, Poland
[b] Department of Experimental Physics, Debrecen University, Bem Ter 18a, 4026 Debrecen, Hungary
[c] Institute of Physics, J. Dlugosz University, Al. Armii Krajowej 13/15, Czestochowa, Poland
[d] Institute of Physics, University of Tartu, Ravila 14C, Tartu 50411, Estonia
[e] Institute of Applied Physics, Military University of Technology, Kaliskiego 2, 00-908 Warsaw, Poland
[f] College of Sciences, Chongqing University of Posts and Telecommunications, Chongqing 400065, PR China
[g] Institute for Nuclear Research, Hungarian Academy of Sciences (MTA Atomki), H-4026 Debrecen, Bem ter 18/c, Hungary

HIGHLIGHTS

- UV–VIS absorption, excitation and time-resolved luminescence spectra are done.
- The ratio of crystal field strength to Racah parameter indicates a borderline case between strong and weak field.
- The sample have some SHG capabilities that can be increased by poling the glass by proton implantation.

GRAPHICAL ABSTRACT

Time-resolved spectra of BiBO:Cr 4 at.% glass luminescence.



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ABSTRACT

Synthesis, spectral properties and photoinduced nonlinear optical effects of chromium-doped BiB_3O_6 glass are studied in the present paper. Absorption, excitation and time resolved luminescence spectra are presented and luminescence decay behavior is discussed. Detailed analysis of the obtained spectra (assignment of the most prominent spectral features in terms of the corresponding Cr^{3+} energy levels, crystal field strength *Dq*, Racah parameters *B* and *C*) was performed. A weak photostimulated second harmonic generation signal was found to increase drastically due to poling by proton implantation in the investigated sample.

Introduction

Borate glasses may be considered as promising materials which can accept the transition metal and rare earth ions as efficient dopants [1–3]. The borate glasses are characterized by relatively high phonon frequencies, which enhances the efficient interaction with the localized energy levels of impurities. As it has been shown by the calculations performed in Ref. [4], such contribution may be mainly attributed to $[BiO_4]^{5-}$ anionic group.

In the present work we will perform the complex studies of the absorption, excitation and the photoluminescence spectra for the

* Corresponding author.

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Cr^{3+} ions doped BiB_3O_6 glasses (BiBO). It is well known that the Cr ions may change their valence states in such matrices, which is crucial for the formation of the local charge density acentricity, finally responsible for the second order optical effects like the second harmonic generation (SHG). Valuable information concerning the distribution of the electron density of the Cr^{3+} dopant ion can be derived from the analysis of luminescence spectral kinetics.

Monoclinic α-BiBO crystallographic phase has been widely studied due to its high nonlinear optical parameters, especially SHG [5]. It was shown that α-BiBO cannot be efficiently doped with rare earth ions [6]. On the other hand, significant second order optical susceptibilities were found for rare earth doped BiBO glass nanocomposites and partially crystallized BiBO glass [7,8]. Under normal conditions the SHG effects require some acentricity and they cannot be observed in glasses. However, external laser stimulation at some specific conditions may break the centrosymmetry and the observation of the SHG becomes possible. In the present work we study the SHG stimulated by external light and by proton implantation. Presence of Cr^{3+} ions with some localized electronic levels favors enhancement of such kind of effects.

Materials and methods

Glass preparation and doping

BiBO:Cr glass was obtained by means of high-temperature synthesis from stoichiometric amounts of B_2O_3 (Merck Suprapur), Bi_2O_3 (Aldrich, 99.999%) and Cr_2O_3 (Aldrich 99.99%). Since the chromium ions substitute for the bismuth ions, a proper molar content of Bi_2O_3 was replaced with Cr_2O_3. To remove the absorbed water, both Bi_2O_3 and Cr_2O_3 powders were dried for 24 h at 500 °C and 800 °C, respectively. Boron oxide was molten first in a platinum crucible at elevated temperatures up to 1000 °C for several hours to remove the absorbed water and therefore to secure known composition of synthesized glass. By weighing the crucible we were able to find the mass of B_2O_3. In the next step proper amounts of Bi_2O_3 and Cr_2O_3 powders were dissolved in the molten B_2O_3. The synthesis was carried out at approximately 850 °C. The melt was homogenized with use of a platinum stirrer for several hours until it became totally transparent. Homogeneous melt was poured onto Pt/Au5% glass forming plate and rapidly cooled below 400 °C. The plates were cut out from the formed glass with use of wire saw and polished before optical measurements. For further spectroscopic measurements the BiBO:Cr 4 at.% glass plates were prepared.

Optical measurements

Photoluminescence (PL) emission and excitation spectra as well as luminescence decay kinetics were examined. For measurement of the PL emission spectra and decay kinetics, the pulsed (pulse duration 10 ns) third harmonic of the Nd:YAG laser operating at 355 nm and 10 kHz was applied as an excitation source. The pulse energy was equal to about 1 μJ. A laser beam was focused in a backscattering geometry onto about 1 mm^2 spot on the sample's surface. The spectra were recorded by a spectrograph (Andor SR-303*i*) equipped with an intensified charge coupled device (Andor DH-501) with spectral resolution up to 1 nm. This detector could be used to acquire time-resolved PL spectra with time-resolution down to 5 ns. Decay kinetics was estimated by integration of time-resolved spectra. For measurements of the PL excitation spectra, the 150 W Hamamatsu Xenon lamp was used in combination with a monochromator (MDR-23, spectral width 2 nm) as the tunable excitation source. A 1 × 1 mm^2 area was irradiated with a proton beam forming a pattern of parallel ion-implanted 10 μm wide strips separated by 10 μm gaps. The SHG signal was measured at the ion implantation spot and on unplowed area on the sample. The SHG measurements were performed by 15 ns Nd:YAG laser beams on the output SHG was detected by a Hamamatsu photomultiplier with green filters. The output signal was analyzed by the 1 GHz Tectronics oscilloscope.

Results and discussion

The excitation spectrum is presented in Fig. 1. There are two clearly visible spectral maxima situated at 340 nm and 450 nm, which can be assigned to the $^4A_2$–$^4T_1$ (^4P) and $^4A_2$–$^4T_1$ (^4F) transitions of the octahedrally coordinated Cr^{3+} ions, respectively. The most prominent spectral feature attributed to the $^4A_2$–$^4T_1$ (^4F) transitions begins from 380 nm and achieves its maximal value at about 450 nm. The space non-homogeneity in distribution of the rare earth did not exceed 0.9% following the absorption controlee.

The absorption spectrum (Fig. 2) clearly demonstrates a wide principal spectral band centered at about 620 nm assigned to the $^4A_2$–$^4T_2$ (^4F) transition of the Cr^{3+} ions. There are also visible spectral features with considerably lower intensities at 669 and 697 nm, arising from the $^4A_2$–$^2T_1$ (^2G) and $^4A_2$–^2E (^2G) spin-forbidden transitions, respectively.

Analysis of the spectra shown in Figs. 1 and 2 allows to estimate the main spectroscopic parameters (crystal field strength *Dq*, Racah parameters *B* and *C*), which determine the general energy level scheme of trivalent chromium in the studied sample [9–11]. The energy of the $^4A_2$–$^4T_2$ (^4F) transition of the Cr^{3+} ions is known to be equal to 10*Dq* [12]. The value of the Racah parameter *B* can be evaluated from the following equation:

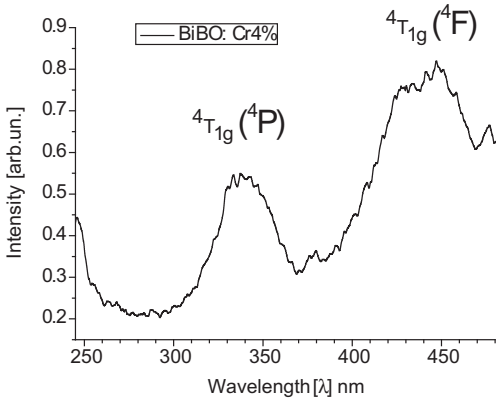

Fig. 1. Excitation spectrum of BiBO:Cr 4 at.% glass measured at 710 nm.

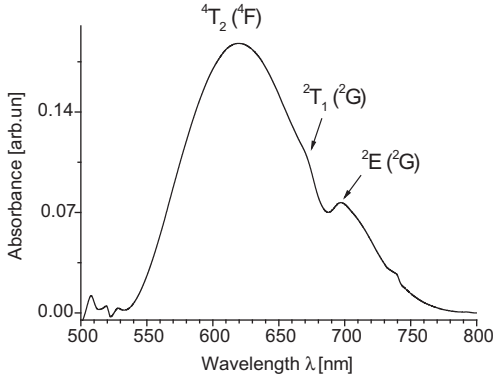

Fig. 2. Baseline-corrected absorption spectrum of BiBO:Cr 4 at.% glass.