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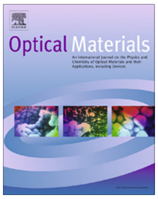

Low temperature phase barium borate: A new optical limiter in continuous wave and nano pulsed regime

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ABSTRACT

Low temperature phase barium borate was synthesized by hydrothermal method. XRD analysis confirms the formation of γ-BBO or hydrated barium polyborate ($Ba_3B_6O_9(OH)_6$) which crystallizes in monoclinic system in the P2/c space group. The molecular structure analysis shows the presence of dominant BO_4 unit and the hydrated nature of material. γ-BBO exhibits sharp absorption edge at 202 nm and highly transparency in the UV–Visible–NIR region. The peak at 347 nm in the emission spectrum is due to the presence of self-trapped exciton. The third order nonlinear optical properties and limiting behavior of low temperature barium borate in both pulsed and continuous wave regime were studied. The effective 2PA absorption coefficient of γ-BBO under ns pulse excitation is estimated to be 0.38×10^{-10} m/W. The nonlinear absorption coefficient, refractive index and optical susceptibility of the material in cw regime were found to be in the order of 10^{-5} m W^{-1}, 10^{-12} m^2 W^{-1}, 10^{-6} esu respectively. In both regimes, low temperature phase barium borate exhibits better optical limiting properties than high temperature phase β-BBO.

1. Introduction

Research on the borate materials has been constantly prompted due to their potential applications in manufacture of nonlinear optics (NLO), luminophore, radiation shielding, etc. [1]. In borate family, barium borate (BBO) is the most widely used member as NLO material due to its large nonlinear optical coefficient (6 $d_{eff.}$ than KDP at 1.06 μm) and higher laser damage threshold (5 GW/cm^2 for 10 ns pulses at 1064 nm) [2]. In BBO the origin of large nonlinear optical susceptibility arises from the anionic structural units and as boron atoms has two kind of co-ordination, a boron atom co-ordinate with three oxygen atom to form triangle [BO_3] unit and with four oxygen atom to form tetrahedral [BO_4] unit. The network of interconnected [BO_3] and [BO_4] forms infinite chains of [B_3O_6], [B_3O_3] anionic groups whose negative charge is compensated by the Ba^{2+} cations and hence resulting in diversity of structures [3]. Due to this versatility of arrangement of anionic units, barium borate can be obtained in three distinct crystalline phases α, β and γ. Depending upon the reaction temperature, low temperature centrosymmetric γ-BBO (below 400 °C), non-centrosymmetric β-BBO (between 400 and 950 °C) and centrosymmetric α-BBO (above 950 °C) can be obtained. It is well known that β-BBO crystals are the most intensively investigated for their waveguide efficiency based frequency converters, modulators and switches [4]. Also high temperature α-BBO glassy borates have been thoroughly studied in radiation shielding, solid state lasers, solar energy convertors and so on [5]. For the past few decades, although high temperature phase of BBO was thoroughly investigated, low temperature γ-BBO remained unexplored. γ-BBO is also called as hydrated barium polyborate having the molecular formula, $Ba_3B_6O_9(OH)_6$ [6]. Very recently, the synthesis of low temperature phase of barium borate by hydrothermal method was reported [7,8]. Even though γ-BBO crystallizes in centric system, the crystal structure mimics the salient features of β-BBO and hence it will possess interesting third order NLO properties.

The drastic advancement in the field of high intense lasers in research and technology demands protection for human eye and optical components from intense laser beam. Safeguarding photosensitive components can be achieved by NLO process like optical limiting which exhibit decrease in transmitted intensity with increase in incident light intensity [9]. An ideal optical limiter must have an ability to fulfill the specification like broadband limiting efficiency over whole visible spectrum and temporal efficiency from nanosecond (ns) pulses to continuous wave (cw) regime [10]. Among the available NLO materials, only few show the wide dynamic range of limiting behavior at pulsed and cw regime. In most of the materials, the optical limiting mechanisms exist in

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number of forms such as two/three photon absorption, reverse saturable absorption, free carrier absorption, nonlinear scattering and thermal defocusing/scattering [11]. In ns pulse lasers, the nonlinear absorption involves electronic process explained with triplet level (3-level) or five level (5-level) model. Under cw laser illumination, the material exhibits the optical nonlinearity in the form of refractive rather than absorptive [12]. Earlier report shows β-BBO exhibits excellent limiting behavior in both ns pulse and cw regime [13]. Impressed by the crystal structure similarities between γ-BBO and β-BBO, this article reports the preparation of low temperature phase of barium borate by organic free hydrothermal technique. Also the structural, optical and third order nonlinear optical properties of the material will be discussed. The limiting behavior of γ-BBO in both ns pulsed and cw regime is analyzed in detail.

2. Experiment

As preparation of metal borates by high temperature methods like melt and flux are expensive, low temperature hydrothermal synthesis can be an alternative efficient method for the bulk production in industrial sectors. In the preparation of low temperature phase of BBO, analar grade 10 mmol of $BaCl_2{\cdot}2H_2O$, 15 mmol of H_3BO_3 and 20 mmol of NaOH were dissolved in 60 ml distilled water at room temperature (30 °C). The solution was mixed completely through continuous stirring and the homogeneous solution was transferred into a teflon lined stainless steel autoclave setup. The autoclave setup was maintained at 160 °C for 8 h, without stirring or shaking and was allowed to cool to room temperature (30 °C) naturally. The settled precipitate was washed with distilled water and ethanol for several times to achieve purity. The obtained powders were dried at 50 °C for 3 h [7].

The phase and preliminary identification of the product was investigated by PAN Analytical X-ray powder diffractometer employing a scanning rate of $0.02^\circ s^{-1}$ in the 2θ range from 15° to 80°. The FEI Quanta FEG 200 High Resolution Scanning Electron Microscope with Energy Dispersive X-ray spectroscopy (FESEM-EDS) was used to study the elemental composition of the prepared materials. The optical absorption spectrum was collected for dispersed γ-BBO using UV–Vis–NIR Perkin Elmer Spectrophotometer. The room temperature (30 °C) emission studies were carried out using a Perkin Elmer LS 55 luminescence spectrometer. The third order nonlinear optical properties and optical limiting behavior of the sample were studied by Z-scan experiment using two different laser sources, short pulse excitation with a Q-switched frequency doubled Nd:YAG laser (532 nm, 5 ns, 100 μJ) and continuous excitation with a diode pumped Nd:YAG laser (532 nm, 50 mW) (Fig. 1). A simple schematic diagram of Z-scan experiment setup used is as shown in Fig. 1. The sample was mounted on the microprocessor controlled translation stage and the transmittance was measured by varying the position along *Z* axis with respect to the focal plane. A pyroelectric laser energy detector and digital power meter was used to measure the transmitted energy at each *Z* position in ns pulse and cw excitations respectively. Moreover to enable the complete thermal relaxation of the sample under pulsed excitation, the interval between two successive laser pulses was always kept sufficiently large before the arrival of the next pulse.

3. Results and discussion

Fig. 2 shows the recorded XRD pattern of the prepared sample where the peaks were indexed with JCPDS no: 01-071-2501. The pattern clearly confirms the formation of γ-BBO or hydrated barium polyborate, $Ba_3B_6O_9(OH)_6$ which crystallizes in monoclinic system with centric P2/c space group. Using AUTOX software, the lattice constants were evaluated to be $a = 6.98(2)$ Å, $b = 7.13(1)$ Å, $c = 11.92(2)$ Å and volume 594.32(1) Å^3 [6,7]. However no traces of β-BaB_2O_4 which crystallizes in hexagonal system with space group of R3C having lattice constants of $a = b = 12.507$ and $c = 12.73$ Å [13] were observed. The presence of high intense peaks and the absence of any traces of β-BBO indicate the single phase formation of the crystalline γ-BBO. The crystal structure of γ-BBO is composed of $[B_6O_9(OH)_6]_n^{6n-}$ built up by non-planar six membered B_3O_3 rings. The anionic infinite chains are compensated by the Ba^{2+} cations residing between the adjacent sides of the chain through the electrostatic interactions holding the chain structure together. The independent two Ba atoms are coordinated with ten oxygen atoms to form distorted tetrahedral BO_4 groups [6]. However in the case of β-BaB_2O_4 the structure is composed of planar six membered anionic (B_3O_6) boroxyl ring made up of three planar BO_3 units which are bonded ionically through barium ions. Hence the basic difference between the two phases is that non-planar BO_4 units are dominant in the γ-BBO while planar BO_3 units are dominant in β-BBO. The recorded EDS image of γ-BaB_2O_4 shown in Fig. 3 clearly indicates the presence of Ba and O with atomic weight distribution of 29.08% and 70.92% respectively. This reveals that the prepared sample was free from other impurities.

The recorded FTIR spectrum of γ-BaB_2O_4 is shown in Fig. 4. The strong peaks at 858, 923, 997 and 1074 cm^{-1} are due to the B–O stretching vibration of tetrahedral BO_4 units. The band at 715 cm^{-1} is assigned to the B–O–B bending vibration of bridge B atoms. The sharp peak at 552 cm^{-1} is due to the contribution of Ba–O bonds. The peaks observed at 1450 cm^{-1} attributes the stretching vibration of BO_3 units [14]. Thus the FTIR spectrum confirms that the boron atoms are tetrahedrally coordinated with oxygen atoms. The broad band observed at 2750–3500 cm^{-1} indicates the presence of O–H bonds and the hydrated nature. Comparing the FTIR spectra of γ-BaB_2O_4 with that of β-BBO, it can be concluded that BO_4 units are dominated in the structure of γ-BBO whereas BO_3 units are dominant in β-BBO [13].

The solid state absorption spectrum of the prepared material is shown in Fig. 5. It shows that the material exhibits sharp absorp-

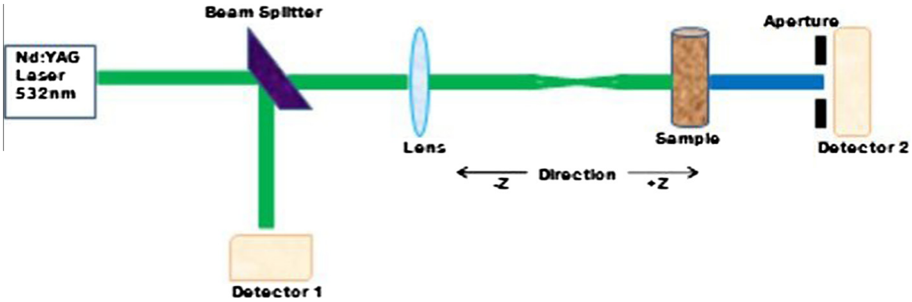

Fig. 1. Schematic representation of Z-scan experimental setup.