

Full length article

Role of reaction time in tuning the morphology and third order nonlinear optical properties of barium borate

T.C. Sabari Girisun^{a,*}, M. Saravanan^a, G. Vinitha^b^a Nanophotonics Laboratory, School of Physics, Bharathidasan University, Tiruchirappalli 620024, India^b Division of Physics, School of Advanced Sciences, Vellore Institute of Technology (VIT), Chennai 600127, India

ARTICLE INFO

Keywords:

Nanostructures
Chemical synthesis
Electron microscopy (SEM)
Optical properties

ABSTRACT

Single crystalline nanoclusters and nanorods like structure of barium borate (β -BaB₂O₄) were synthesized by organic free hydrothermal method at various reaction times of 8, 24 and 48 h. XRD shows the formation of pure and single phase of β -BaB₂O₄ with improved crystallinity at elevated reaction time. β -BaB₂O₄ crystallizes in hexagonal system with lattice parameter $a=b=12.53$ Å and $c=12.72$ Å. The surface morphology picturizes the formation of nanoclusters and rod structures with several micrometer length and nanometer diameter. By increasing the reaction time and due to prolonged pressure, aggregation followed by elongation resulted in the transformation of nanoclusters into rod like structure. The nanostructured barium borates possess strong UV absorbance and wide optical window. The nonlinear optical studies by Z-scan technique shows the material to possess saturable absorption and self-defocusing nature. A strong variation in third order nonlinear optical parameters with change in the morphology of β -BaB₂O₄ was observed. Also β -BaB₂O₄ rod like structure is identified to be more efficient optical limiters in the green regime of continuous wave lasers.

1. Introduction

Borate based materials are best known for their nonlinear optical (NLO) properties, among which barium borate [1–5] (β -BaB₂O₄) plays a major role due to its high laser damage threshold (5 GW/cm² for 10 ns, 1064 nm) and large transparency range (190–3500 nm). Literature shows that nanostructures of borates show enhanced properties than its bulk form and to mention a few, aluminum borate nanowires [6] provide high mechanical strength, magnesium borate nanowires [7] offers high resistance to corrosion and barium borate nanoplates [8] showed improved temperature stability. In the NLO studies, nanoplates [9] and network like structures [10] of β -BaB₂O₄ provide 5 times larger SHG signals and wider transmission than its bulk β -BaB₂O₄. Moreover nanorods of β -BaB₂O₄ exhibit high SHG intensity of about 1.2 times than that of network like structures [11]. Similarly 1D of β -BaB₂O₄ like micro and nano wires offer enhanced field intensity, good optical waveguiding capabilities than its bulk form [12]. Although plenty of research is focused on the single crystals of barium borate, recent research is focused on the investigation of 1D nanostructures of β -BaB₂O₄. This is because the intrinsic anisotropic nature of 1D nanomaterials results the nanoscale confinement in two dimensions and so they are capable of efficient transport of electrons and optical excitations. Among several methods available for the

preparation of 1D barium borate nanostructures, hydrothermal method is more advantageous owing to the fact that nanocrystals of barium borate aggregate severely due to its high surface energy [9–15]. Also the morphology of the 1D nanostructures can be tuned by altering the experimental parameters such as concentration, pH, reaction time, temperature, stirring rate and atmosphere in hydrothermal method [12].

The rapid advancement in the field of high intense lasers in research and technology insist the need for limiters which can protect human eye and optical components from intense laser beam. In recent years, usage of diode pointer laser that operate in visible region (400–760 nm) with power ranges from 1 to 5 mW is becoming widespread. Moreover, for human eye safety with visible continuous wave (cw) diode laser of 5 mW intrabeam expose requires a filter of Optical Density 0.7 for exposure in the order of 0.25 s. Also with technological advancements, intense pointer lasers are available now in the market and one such pointer (imported from Russia) laser is a diode-pumped frequency doubled Nd:YAG laser operating at 532 nm which produces a beam of average power 0.85 mW (envelope of 40 ns pulses of 0.5 μ J/pulse 1.7 kHz). The power emission from this pointer laser exhibits 12 times higher energy per pulse than the Maximum Permissible Exposure (MPE) suggested by ANSI Z136 [17]. Hence it's undoubtedly true that the protective material called as power limiters are in urgent

* Correspondence to: Nanophotonics Laboratory, School of Physics, Bharathidasan University, Tiruchirappalli 620024, India.
E-mail addresses: sabargirisun@bdu.ac.in, sabari.girisun@gmail.com (T.C. Sabari Girisun).

need to safeguard the human eyes from the hazardous lasers. In the search of effective power limiters, 1D β -BaB₂O₄ can be a suitable material as it possesses wide optical window, fast response time and high laser damage threshold than its bulk form and other borate materials. The present paper reports on the preparation of 1D barium borate by hydrothermal method and the study of nonlinear transmission, nonlinear absorption and optical limiting effects of nanostructured barium borate materials by Z – scan experiment [18] using Nd:YAG laser (532 nm, 50 mW).

2. Experiment

The preparation of nanostructures by hydrothermal technique allows altering experimental parameters such as concentration of precursor, reaction temperature and reaction time for tuning the morphology of the product in nanoscale [16]. Based on the literature [5], initially the concentration of reactants and reaction temperature was fixed to attain the pure single phase of β -BaB₂O₄. The reaction was carried out at various reaction times, as prolonged heating and pressure favors the formation of one-dimensional structures. Hence in the typical experimental procedure, 18 mmol of BaCl₂·2H₂O, 21 mmol of H₃BO₃ and 24 mmol of NaOH were dissolved in 108 ml of distilled water and stirred for 2 h to form clear solution. Then, the white slurry was transferred into stainless steel autoclave and maintained at 433 K for 8 h. After the reaction, the obtained flocculent precipitate was filtered and washed repeatedly with distilled water and ethanol. In order to alter the morphology of the prepared material, similar synthesis procedure was adopted with the change in reaction time as 24 and 48 h. To achieve the pure β - phase of barium borate, as synthesized powders were heated at 1073 K for 1 h [19].

The phases of the products was investigated by PAN Analytical X-Ray powder diffractometer employing a scanning rate of 0.02°s⁻¹ in the 2 θ range from 20° to 80°. The FEI Quanta FEG 200 High Resolution Scanning Electron Microscope (FESEM) was used to study the surface morphology of the prepared materials. The optical absorption spectra were recorded for β - BaB₂O₄ dispersed in ethylene glycol at room temperature (303 K) with UV- Vis Perkin Elmer Spectrophotometer using 1 cm cuvette. The optical nonlinearity of the samples dispersed in ethylene glycol was studied by Z- scan technique, using diode pumped Nd: YAG laser (532 nm, 50 mW) as excitation source.

3. Results and discussion

Barium borate exist in three crystalline forms; α -BaB₂O₄, β -BaB₂O₄ and γ -BaB₂O₄, and so the preliminary and phase confirmation is initially made by powder XRD analysis. The recorded XRD patterns are shown in Fig. 1. The diffraction patterns of all the peaks were compared with literature and are found to be matching with the β -BaB₂O₄ [JCPDS No. 80 – 1489]. All the peaks were indexed and no other characteristic peaks of any impurity group were observed which shows the formation of pure barium borate. Further analysis shows that the material crystallizes in hexagonal system with lattice parameters a=b=12.53 Å and c=12.72 Å and space group of R₃C [11]. The XRD pattern shows the presence of major characteristic peaks of barium borate at 24° and 26° which corresponds to (300) and (113) plane respectively. With consequent increase of reaction time, the crystallinity of the sample got improved which is observed from the increase in the intensity of XRD peaks and is due to the prolong pressure applied on the precipitate. Significant peak broadening observed in the XRD pattern of the samples compared to that of its bulk form [JCPDS No. 80 – 1489], confirms the reduction in the size. To further elucidate the size reduction, the average crystallite size was estimated by Scherrer formula to be 17 nm, 14 nm, 13 nm for β -BaB₂O₄ obtained at reaction time of 8, 24, 48 h respectively.

The typical morphology of prepared β -BaB₂O₄ shows significant variation in the morphology with increase in reaction time. FESEM

image of the samples prepared at 8 h (Fig. 2a) shows the formation of nanoclusters with size ranging from 65 to 140 nm. The formation of nanoclusters occurs through intermolecular vanderwaals force with which the nuclei aggregate together to form relative larger structure. This is because nanocrystals tend to agglomerate together to decrease the exposed surface area to lower its surface energy. Interestingly, for samples prepared at 24 h (Fig. 2b) aggregation of nanoclusters along a particular direction takes place. Therefore the continuous pressure on the nanoclusters induce elongation to form rod like structure with approximate dimension ~1.5 μ m length and ~900 nm diameter due to the alignment of same type of crystal planes to form a coherent interface to minimize the interface strain energy. Further increasing the reaction time to 48 h, due to the extended pressure the elongated nanoclusters are now well controlled attaching with each other along the fast growth direction to form a long range ordered rod like structure (Fig. 2c) with approximate dimension of ~1.7 μ m length and ~200 nm diameter. Traces of nanowires with approximate dimension of ~1.9 μ m and ~30 nm were also observed which further confirms the mechanism involved in the nanostructure formation. As reaction time increases, growth rate and aggregation decreases, thereby imposing a restriction in the elongation of the rod. However strong reduction in diameter arises due to prolonged pressure and temperature applied throughout its length. The imbalance in the size reduction may also be attributed partially because of Ostwald ripening. A similar morphology change with reaction time was observed for ZnO nanorods [20]. The length to diameter aspect ratio of elongated nanoclusters, nanorods and nanowires are estimated to be 1.5, 8.1 and 63.3 respectively. Thus the SEM images infers that the reaction time is one of the crucial parameter to form the nanostructures [21,22].

The linear optical absorption and electronic transition of the prepared samples were investigated using UV- Vis absorption spectra. In the recorded absorption spectra (Fig. 3), the sample at different reaction time reveals maximum absorption edge around 225 nm. The

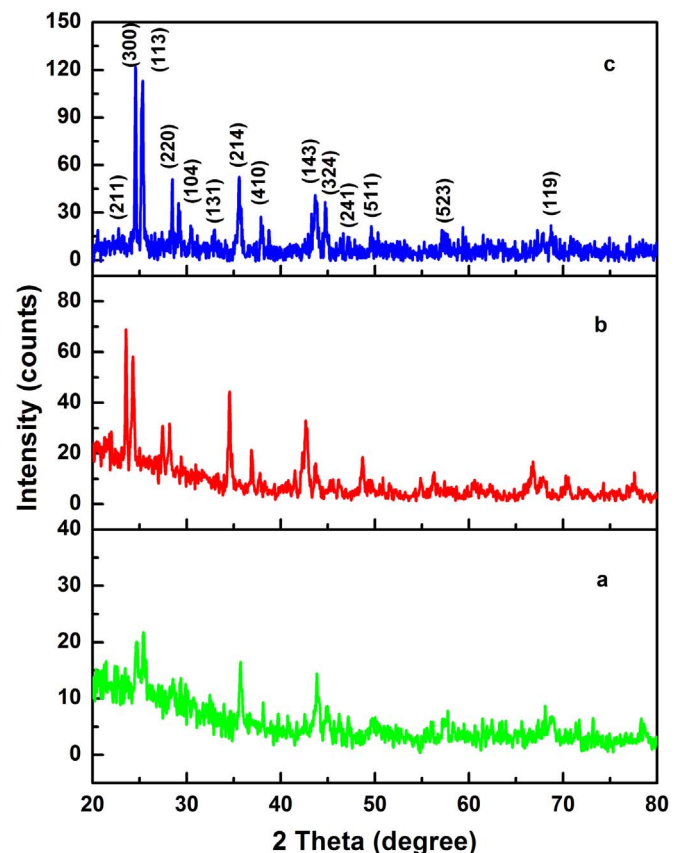


Fig. 1. XRD pattern of the barium borate prepared at (a) 8 h (b) 24 h and (c) 48 h.

Download English Version:

<https://daneshyari.com/en/article/5007629>

Download Persian Version:

<https://daneshyari.com/article/5007629>

[Daneshyari.com](https://daneshyari.com)