Growth of α-BiB_3O_6 crystals by spontaneous nucleation method

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ABSTRACT

Monoclinic Bismuth triborate(α-BiB_3O_6) crystals have been grown by spontaneous nucleation technique. The presence of crystalline α-BiB_3O_6 phase was confirmed by powder XRD method and the functional groups were confirmed by FTIR spectrum analysis. The UV cut off wave length was found to be 356 nm from the reflectance spectrum of UV-Visible-NIR spectral analysis .The optical band gap of the BiB_3O_6 crystal was found to be 3.489eV by Kubelka – Munk method. The second harmonic generation (SHG) efficiency of the sample BiB_3O_6 was tested by Kurtz- Perry powder technique.

Key words: Powder XRD, UV-band gap, FTIR- analysis, NLO

1. INTRODUCTION

Nonlinear optical crystals are key materials for the development of Laser science and technology because this kind of materials will change the frequency of laser beam and modulate it in amplitude and phase [1].KTP is a NLO crystal which has high nonlinear co efficient and a large angular band width. But it suffers from issues such as transmission losses, refractive index changes and cannot be used with high energy lasers because its laser damage threshold is relatively low.

To date KH_2PO_4 (KDP), β- BaB_2O_4 (β-BBO), LiB_3O_5 (LBO) and $KTiOPO_4$ (KTP) have been used for SHG of Nd-type lasers. However all these materials suffer from some sort of limitations such as their maximum available size, hygroscopic or low harmonic generation efficiency [2]. BiB_3O_6 is a NLO crystal which has exceptionally large NLO coefficients and is not deliquescent. It was reported that laser damage threshold of BiB_3O_6 was comparable to high quality LBO [3].

Borate crystals thus have been attracting much attention due to their outstanding linear and nonlinear optical properties. BiB_3O_6 was first found by Levin and Mc Daniel in process of studying the binary phase diagram Bi_2O_3-B_2O_3[4]. Leibertz grew the first BiB_3O_6 single crystal in 1984 [5]. The crystal structure was reported in 1999 by Becker et. al. and also reported top seeded growth of BiB_3O_6 [6-8]. Hellwig et.al. reported NLO co efficient and some linear optical properties of BiB_3O_6 [9]. The highest d_{eff} found in the SHG phase matching direction at 1079.5nm is 3.2 pm/V. This value was higher than those of many other substances being widely used such as KTP, BBO and LBO [10].

In this present work, Bismuth triborate crystals were grown by spontaneous nucleation method. The crystals were characterized XRD, FTIR, UV and Nonlinear optical studies.

2. EXPERIMENTAL PROCEDURE

2.1 Synthesis:

The sample was prepared by using bismuth oxide (Bi_2O_3 99.9% Sigma Aldrich) and boric anhydride (B_2O_3 99.9% Sigma Aldrich). The raw materials were taken in stoichiometric ratio 1:3 as per phase diagram reported by Levin and McDaniel [4]. The appropriate amounts of raw material were weighed in electrical balance. The weighed materials were ground and mixed thoroughly in a mortar, filled in a platinum crucible and then kept in a furnace at 850^{o}C for 24 hours. The reaction process is as follows

$$Bi_2O_3 + 3B_2O_3 \rightarrow 2BiB_3O_6$$

After the reaction the homogeneous solution was cooled to 600^{o}C at 3^{o}C/h.

2.2 Crystal Growth

After synthesis process the samples were again melted at 850^{o}C and then cooled to 710^{o}C at the rate of 5^{o}C/hr. During this process platinum wire was introduced and the melt was stirred well for homogenization. From 710^{o}C the charge was cooled to 690^{o}C at the rate of 3^{o}C/day and the platinum wire was rotated at 5rpm.

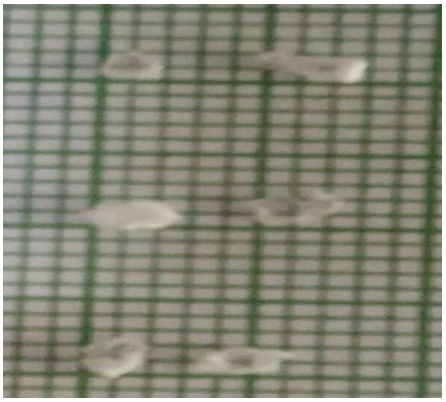

Fig.1. α - BiB_3O_6crystal

At growth temperature tiny crystals were found to be nucleated spontaneously on the surface of the melt and on seed rod. After the formation of considerable number of crystals, platinum wire was then pulled slowlyand the crystals were separated from the solidified melt. Small crystals of (α-BiB_3O_6) of size 2mm X 2mm X 0.5mm (figure 1) were grown successfully by spontaneous nucleation method.

2.3 Characterization

The X-ray powder patterns of the samples were recorded using Rigaku D/max-A X-ray diffractometer (CuKα, λ=1.54434 Å) at the scanning rate of 2 deg/min and 2θ is varied from10–70˚. Fourier Transform Infrared spectroscopy was carried out at room temperature in the range of 4000 – 450 cm−1 using a Perkin Elmer Spectrum two FT-IR/ ATR Spectrometer. The powder form of each sample was placed in the sample holder and the FT-IR Spectrum was recorded by using ATR Diamond Accessory. The optical absorption measurements were made using a Lambda 35 UV Winlab Spectrometer, in the range of 190 - 1100nm.The second harmonic generation (SHG) efficiency of the sample was tested by Kurtz- perry powder technique.

3. RESULT AND DISCUSSION

3.1 Powder X-Ray Diffraction

The Powder-XRD spectrum of BiB_3O_6 crystal is shown in Figure 2. From the Powder-XRD spectrum monoclinic structure (α- BiB_3O_6) was conformed. The diffraction pattern well agreed with the data of standard for α- BiB_3O_6 (COD Data). The cell parameter a, b, c and β values are calculated from powder XRD data. The calculated and reported values are compared in table 1.

Cell parameters	Reported [7]	Present work
a	7.116 Å	7.116 Å
b	4.993 Å	4.993 Å
c	6.508 Å	6.508 Å
α, γ	90	90
β	105.62	105.62

3.2 Fourier transform – IR spectrum

The FTIR spectrum of BiB_3O_6 Crystal is shown in Fig. 3. The peaks appearing at 472,508,537 and 577 are due to the Bi-O bonds in BiO_6 groups. The band observed at 655 and 679 cm^{-1} due to the Bi-O-stretching vibrations in BiO_6 units. The band observed at 679, 726 and 768 $cm^{-1}$are due to the B–O-B bending vibration in BO_3 units. The peaks appearing at 837, 942, 1036 $cm^{-1}$are due to the B–O bond asymmetry stretching of tetrahedral BO_4 units. The peaks at 1123, 1155, 1244, 1282 cm^{-1} are due to stretching vibration of B–O of trigonal BO_3 units [12-14].

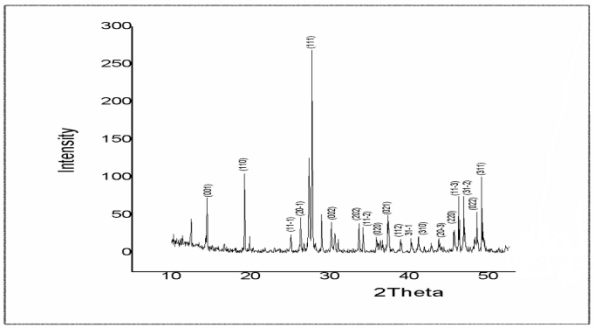

Fig. 2. Powder XRD Pattern of BiB_3O_6 Crystal

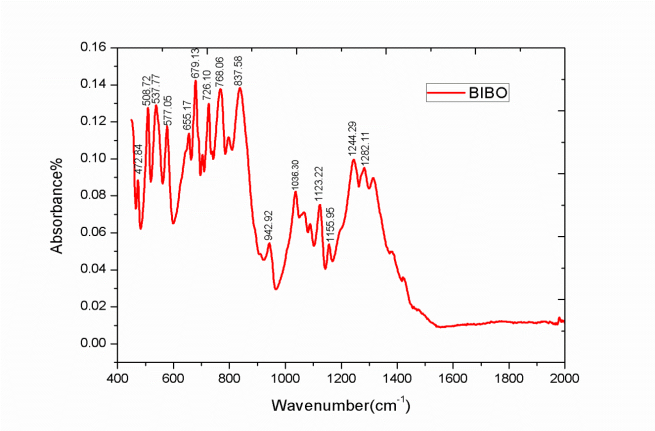

Fig. 3. FTIR spectrum of BiB_3O_6 crystal

3.3 UV–Visible–IR spectral analysis

The UV-visible absorption spectra are very significant for NLO material because a nonlinear optical material must have a wide transparency

window for optical application. The UV-Visible-IR reflectance spectrum of BiB_3O_6 crystal was recorded in the wavelength region 200–1200 nm. The reflectance spectrum of the BiB_3O_6 crystals is shown in Fig.4. The cut of wave length of BiB_3O_6 crystal is found to be 356 cm^{-1}. The optical band gap (E_g) of BiB_3O_6 crystal was calculated by using Kubelka – Munk function as follows.

$$F(R_\infty) = \frac{(1-R_\infty)^2}{2R_\infty} = \frac{k(\lambda)}{s(\lambda)} \propto \alpha = \frac{(h\nu - Eg)^2}{h\nu} \quad \text{----- (1)}$$

From the above equation Band gap is calculated as follows

$$E_g = \frac{(F(R\infty)h\nu)^{1/2}}{(h\nu)} \quad \text{---------- (2)}$$

Where $F(R_\infty)$ is the K–M function or re-emission function, R_∞ is the diffuse reflectance of an infinitely thick sample, $K(\lambda)$ is the absorption coefficient, s(λ) is the scattering coefficient, *h is* Planck constant and *v* is frequency. K-M vs Wavelength graph as shown in Fig. 5.

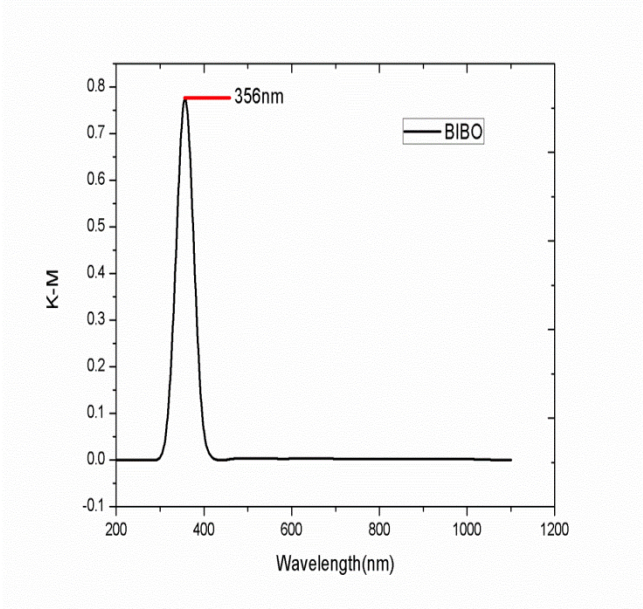

Fig. 5 K-M vs Wavelength graph

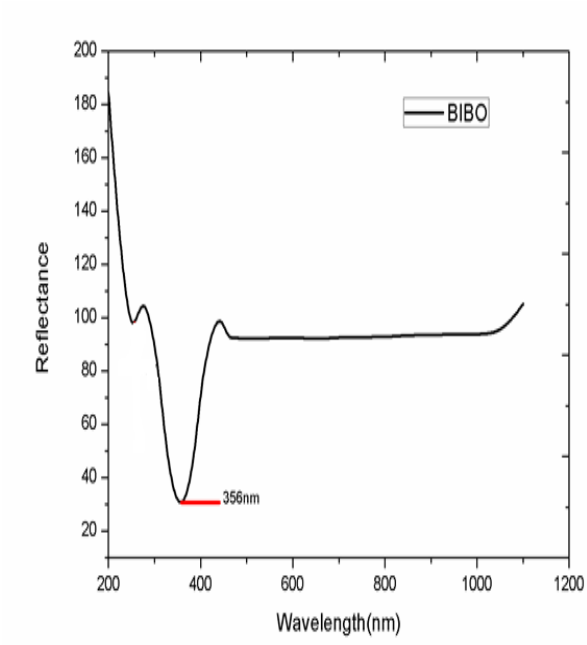

Fig. 4. UV-Visible-IR spectrum of BiB_3O_6crystal

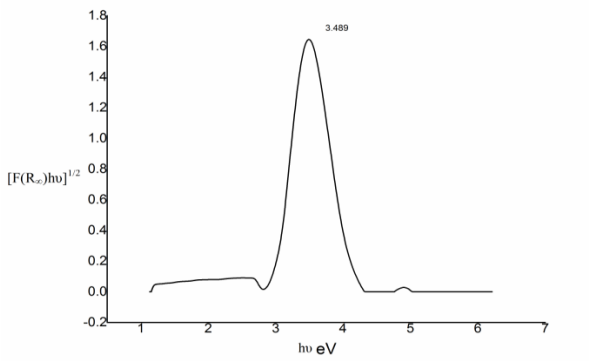

Fig. 6 Band gap energy of BiB_3O_6crystal

The band gap energy was calculated from the plot between $(F(R\infty)h\nu)^{1/2}$ and$(h\nu)$ shown in fig. 6. The optical band gap of the BiB_3O_6 crystal is found to 3.489eV.

3.4 Powder nonlinear optical Studies

The second harmonic generation (SHG) efficiency of the sample $BiB_3O_6$was tested by Kurtz-perry powder technique. The crystal was ground to homogeneous powder and tightly packed in a micro capillary tube and mounted in the path of the Q-switched Nd :YAg laser beam emitting wave length 1064 nm with pulse energy of 1.2mJ/pulse, pulse width of 8 ns and repetition rate of 10 Hz. The generated SHG signal at 532 nm is split from the fundamental frequency using an IR separator. The SHG property of the grown crystal was confirmed by

the green emission of the sample. The measured SHG value is 1.47 times higher than KDP crystal.

4. CONCLUSION

The Bismuth triborate (α- BiB_3O_6) crystals have been grown by spontaneous nucleation method. The grown crystals were characterized by the powder XRD analysis for confirmation of crystal structure. The functional groups of grown crystal were identified from the FTIR spectral analysis. From UV-visible NIR reflectance spectra cut off wave length and optical band gap of grown crystal have been determined. The SHG property of the grown crystal was confirmed by the green emission of the sample in Kurtz - Perry technique.

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