Growth and Characterization of Pure and Yb-Doped Bismuth Zinc Oxyborate ($Bi_2ZnOB_2O_6$)

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Abstract: ***The polycrystalline powder samples of pure and Yb (5 mol %) doped** $Bi_2ZnOB_2O_6$ **(BZOB) in the ternary system** Bi_2O**-ZnO-2**H_3BO_3 **were synthesized by solid state reaction method. These samples were subjected to single crystal growth using handmade Czochralski growth apparatus. Powder samples were subjected to powder X-ray diffraction (XRD) analysis to confirm crystalline phase and study crystal structure, Fourier Transform-Infrared (FT-IR) spectral analysis to identify the chemical bonding and molecular structure of the materials. The melting behaviors of pure and doped BZOB crystals were investigated by differential thermal analysis (DTA). The SHG study shows that the SHG effect has been enhanced by Yb doping. The improvement in the SHG by Yb doping may make the material BZOB prominent of scientific interest for potential application in self frequency doubling laser devices.***

Keywords: bismuth zinc oxyborate, SHG effect, Yb doped $Bi_2ZnOB2O_6$, self-frequency doubling.

1. Introduction

Recently there has been a great interest in the growth of Nd^{3+} and Yb^{3+} doped noncentrosymmetric borate crystals, $GdAl_3(BO_3)_4$: Nd^{3+} (NGAB), $GdCa_4O(BO_3)_3$:Nd^{3+} (Nd:GdCOB), Nd:$YAl_3(BO_3)_4$ and GdCa4O(BO3)3:Yb^{3+} (Yb:GdCOB), Yb^{3+}: $YAl_3(BO_3)_4$ [1-6] as self-frequency-doubling (SFD) materials. The necessary conditions for nonlinear optical crystal to be a self-frequency conversion material are: (1) the crystal must provided a suitable site for activator ions emitting around 1 nm, such as Nd^{3+} and Yb^{3+}, and (2) the crystal must be phase matchable for its laser emission. By combining the nonlinear properties of the matrix crystal and the laser emission due to Nd^{3+} and Yb^{3+}ions, it is possible to generate red, green, blue and even UV laser radiation directly by SFD [7-10] .Such bi-functional materials, in which the laser effect and the non-linear optical phenomena occur simultaneously inside the same host are very attractive for laser devices.Nonlinear optical (NLO) crystals of borate family have attracted considerable attention due to their excellent properties. Many researchers worked on borates materials and investigate a number of binary and ternary compounds, determined their structure, optical and nonlinear optical properties. In 2005 J.Barbier et al [11] first synthesized the new nonlinear optical material, $Bi_2ZnB_2O_7$ in $Bi_2O_3-ZnO-B_2O_3$ ternary system. After that, in 2009 F. Li et tal has grow single crystal of $Bi_2ZnB_2O_7$ with high optical quality and the formula of $Bi_2ZnB_2O_7$ can changed to $Bi_2ZnOB_2O_6$ (BZOB) according to its anionic structure and consider as a new type of oxyborate crystal. In their investigations, they reported, the second-harmonic generation (SHG) effect in BZOB crystal has been three to four times larger than KH_2PO_4 (KDP). It has large optical transmission window, large birefringence and congruent melting nature. [12-14]. These excellent properties make it a promising candidate for nonlinear optical (NLO) materials. The synthesis and growth of Neodymium (Nd) doped BZOB reported in the literature [15] but Ytterbium (Yb) doped BZOB material has not been reported in the literature till date.

In this paper, we made effort for synthesized and grow pureand Yb^{3+}ion doped BZOB material. The powder of pure and doped BZOB polycrystalline material subjected to single crystal growth by using Czochralski technique. The powder of crystals subjected to different characterization technique. The results are discussed and presented in detailed. Such design materials are show excellent properties and assumed to be potential SFD materials. With this aim, we present here the detailed investigations on the synthesis, growth and nonlinear optical properties of pure and Yb^{3+}ion doped BZOB material.

2. Material Synthesis and Crystal growth

Materials

Boric Acid Powder (H_3BO_3) 99.5% Qualigens Fine Chemicals, Zinc- Oxide (ZnO) 99% Qualigens Fine Chemicals, Bismuth Oxide (Bi_2O_3) 99.9% Acros Organics and Yetterbium Oxide (Yb_2O_3) 99.9% LOBA CHEMLE. All chemicals purchase from Fisher Scientifics, Mumbai.

Synthesis

A polycrystalline powder sample of pure and Yb doped BZOB were synthesized in two step by solid-state reaction techniques. In first step, the raw materials Bi_2O_3, ZnO, H_3BO_3 and Yb_2O_3 were used as it is without any purification. As per the following chemical reaction,

$Bi_2O_3 + ZnO_3 + 2H_3BO_3 \rightarrow Bi_2ZnOB_2O_6 + 3H_2O\uparrow$

$(0.05)\ Yb_2O_3 + (0.95)\ Bi_2O_3 + ZnO_3 + 2H_3BO_3 \rightarrow$ Nd: $Bi_2ZnOB_2O_6 + 3H_2O\uparrow$

A stoichometric ratio of ingredients were mixed and ground by using agate mortar. Both mixtures were kept in silica crucible separately and place in homemade programmable high temperature furnace for heat treatment. The crucibles heated slowly up to 500^o C and hold at this temperature for 8 h, and then cooled. In second step, remove these powders from crucible and ground well again and heated at 630^o C for 20 h and cooled. The materials were ground and subjected to powder XRD and DTA analysis. A single-phase powder of pure and Yb doped BZOB were obtained. There were no changes observed in the X-ray powder diffraction pattern due to further heat treatment.

Crystal Growth

The crystal growth experiments were carried out in a homemade electric resistance furnace. Polycrystalline samples of pure and Yb doped BZOB were packed into a crucible separately. Firstly, the pure BZOB packed platinum crucible was placed in the growth furnace. The temperature was raised to 900 ^{o}C and held for 24 h to assure the solution melted completely and homogenously and then quickly cooled to 690^{0}C. Meanwhile, platinum wire as a seed was introduced into liquid surface at this temperature. During the period of growth, the cooling rate and rotation rate were 5^{0}C/day and 15 rpm, respectively. When the growth process ended, the crystal was drawn out of the surface of the solution and cooled to room temperature at a rate of 20^{0} C/h. As a result, transparent BZOB crystal was obtained in four days. Similar procedure was adopted to grow single crystal of Nd and Yb doped BZOB as grown crystals shown in Figure 1.

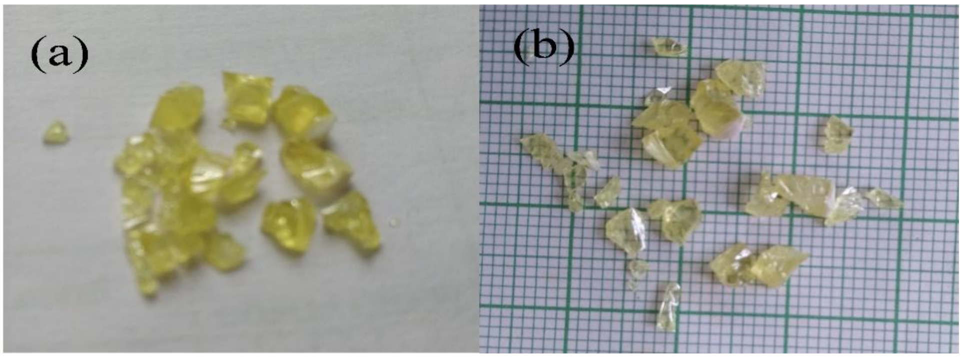

Figure 1 (a) Single crystal of pure BZOB, (b) Yb doped BZOB

3. Results and Discussion

3.1 Structural studies of pure, Nd and Yb doped BZOB using XRD

The fine powder of grown crystals were subjected to X-ray powder diffraction (XRD) analysis, to study the structural and morphological characterization of pure and Yb doped BZOB crystals. The powder XRD patterns of pure and doped BZOB crystals recorded by X-ray diffraction (XRD) using Rigaku Diffractometer Miniflex II with nickel filtered CuKα radiation (λ=1.5406 Å) in the present study. The XRD spectra of both samples are recorded and shown in the Fig. 3.2. The XRD peaks of the samples were indexed using software Powder X [16]. The lattice parameters and cell volume of pure and doped BZOB crystals are given in Table 1. Pure and doped BZOB are positive biaxial optical crystals crystallizes in the orthorhombic system, space group Pba2. The lattice parameters evaluated in the present study are in well agreement with those reported earlier [12]. The same crystal system and space group with very slight variation in the lattice parameters in doped crystals observed. It may be due to the distortion caused locally inside the crystal by inclusion of dopant. Miller indices, inter-planer spacing (observed and calculated) and intensity of Pure and Yb doped BZOB crystals are given in Tables.

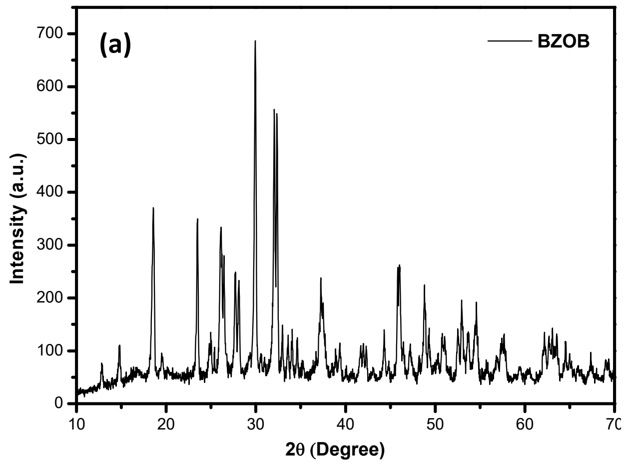

Figure 2: Powder XRD pattern of pure BZOB crystals.

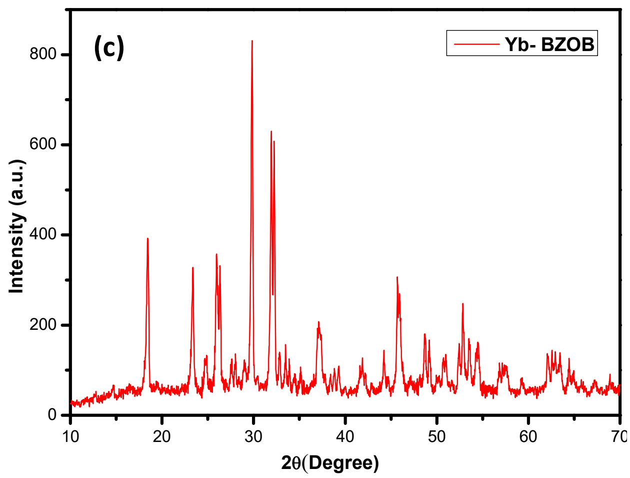

Figure 3.2: Powder XRD pattern of Yb doped BZOB crystals.

3.2 FT-IR Study of pure, Nd and Yb doped BZOB crystals.

Powder samples of pure and doped BZOB crystals were subjected to Fourier Transform-Infrared (FT-IR) spectral analysis to identify the chemical bonding and molecular structure of the materials. FT-IR spectra of pure and doped BZOB crystals were recorded in the transmission mode using IR double beam spectrophotometer, 8400S-Shimadzu, Japan. The peaks assignments are listed in the Table 3.5. The FTIR spectrum of the as grown crystals is shown in Fig. 3. For triangular BO_3 group, the vibrations are in the range between 450–650 cm^{-1} (in-plane bend), 700–900 cm^{-1} (out-of-plane bend), 900–1000 cm^{-1} (symmetric stretch of B–O) and 1100–1400 cm^{-1} (asymmetric stretch of B–O). The peak observed at 500 cm^{-1} is due to the stretching mode of ZnO [17-18]. Hence, It is clear that, BO_3 is the basic structural units of crystal system $Bi_2ZnOB_2O_6$. There are another broad peaks observed at 600cm^{-1} due to symmetric stretching motions in B–O–Bi and B–O–Zn bonds and the peak at 920cm^{-1} due to asymmetric stretching motions in B–O–Bi and B–O–Zn bonds. On the other hand, the entire crystallized samples shows several sharp and weak Peaks together. Hence, it is confirmed that, in $Bi_2ZnOB_2O_6$ crystal Octahedral BiO_6 units, tetrahedral ZnO units, BO_3 and BO_4 units are present. ZnO_4 units and BO_3/BO_4 units are connected through a corner-shared bonding, i.e., the presence of B–O–Zn bonds, and are creating layers. The $Bi_2ZnOB_2O_6$ crystalline phase is, therefore, constructed from the stacking of BiO_6, ZnO_4, BO_3, and BO_4 units [19-21] .

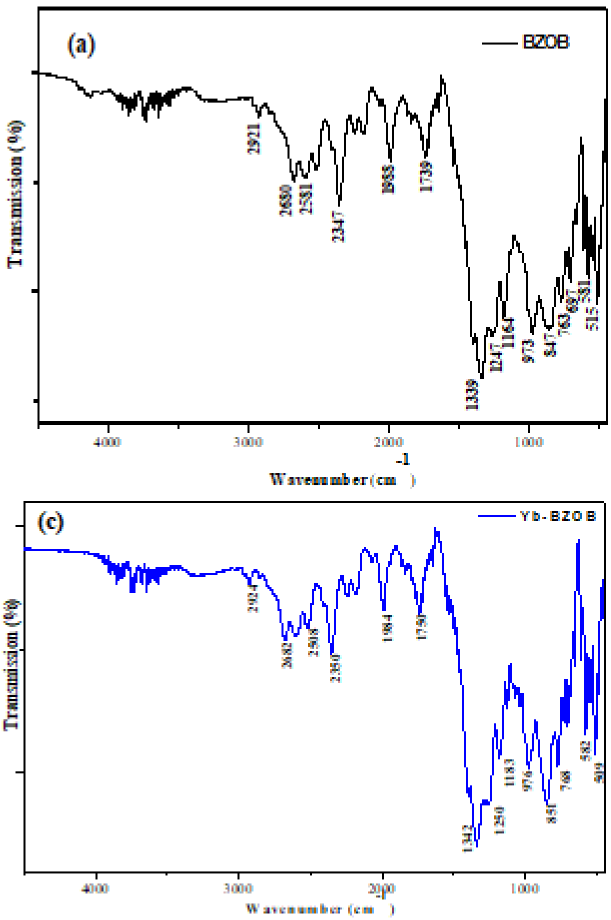

Figure 3.3: FT-IR peaks of (a) pure (b) Nd and (c) Yb doped BZOB crystal

3.3 Differential Thermal Analysis (DTA)

The melting point of pure, Nd and Yb doped BZOB crystals were investigated by differential thermal analysis (DTA) using a NETZSCH STA 449C simultaneous analyzer under static air. The sample and reference (Al_2O_3) were enclosed in Pt crucibles, heated from room temperature to 900^0 C at a rate of 20^0 C/min. The DTA curve of pure, Nd and Yb doped BZOB crystals are shown in following figure. It shows two endothermic peaks at 673 and 698°C on heating curve. The temperature corresponds to the second peak well to the melting temperature, which has reported in the literatures [25-28] and accounts for the complete melting of the sample. But, the first endothermic peak is not reported in the literature and could account for some incongruent character of the samples or could be related to the presence of the parasitic phase revealed by X-ray diffraction one. To verify that BZOB melts congruently, BZOB compound powder (2 g) was put into a platinum crucible and heated to 900° C, then slowly cooled to room temperature the typical thermo gram as shown in Fig3.8. It shows one exothermic peaks at 698°C on cooling curve. Which confirm that BZOB melts congruently at 698°C and has no phase transition below its melting point.

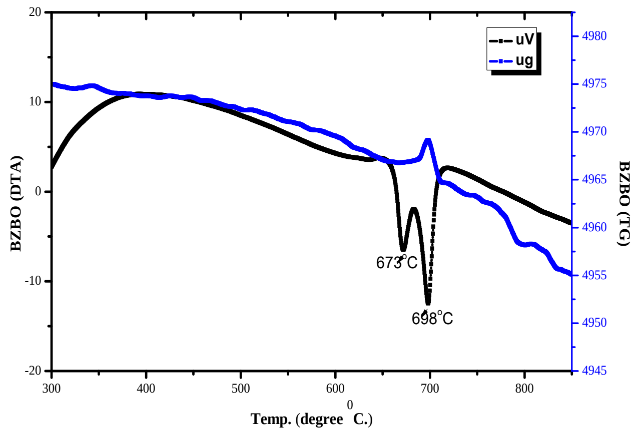

Figure 3.8: TG-DTA study of Pure BZOB

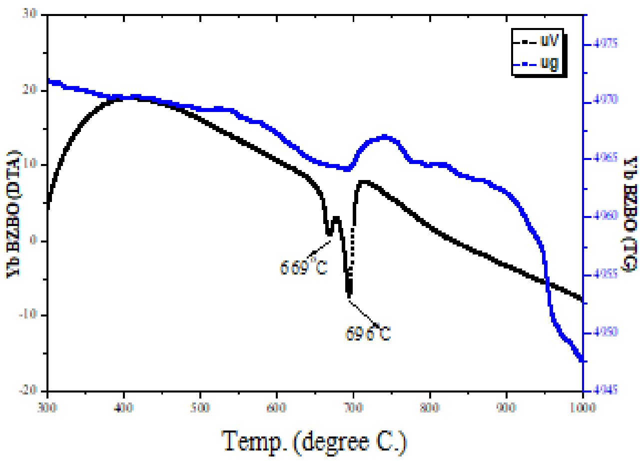

Figure 3.10: TG-DTA study of Yb BZOB

Taking in to account the single phase character observed by X-ray diffraction, the shape of the DTA trace suggests either a slight incongruent behavior or a phase transition not mentioned in the literature. The melting and solidification behaviors of BZOB were measured by differential thermal analysis (DTA) using flowing N2 as the purge gas. The ground crystal powder, which weighed around 10 mg, was placed in a platinum pan. The heating and cooling rate was 10^0 C/min in the temperature range from room temperature to 900^0 C. Fig3.9. presents the DTA curve of BZOB. It shows one endothermic peak at 692^0 C on the heating curve and one exothermic peak on cooling curve at 630^0 C, which confirm that BZOB melts congruently at 692^0 C and has no phase transition below its melting point. The heating curve is accordant with the result of reference [26], while the cooling curve present here has not been obtained previously.

Table 3.7: Melting point of pure and doped crystals

Crystals	Melting point
Pure BZOB	698°C ,
Yb:BZOB	697°C

Second Harmonic Generation Efficiency

The well known Kurtz and Perry technique (Kurtz and Perry 1968) [27]was used to study the NLO property of as grown pure, Nd and Yb doped single crystals from polycrystalline powder materials. In this technique, Q switched Nd:YAG laser having 1064 nm wavelength is used to test the Second Harmonic Generation (SHG) property of the pure , Nd and Yb doped BZOB crystals. Pulse energy of 6 mJ/s with pulse width of 8 ns and repetition rate of 10 Hz is used [28-32]. The output-doubled frequency SHG signal was separated from fundamental ones by placing an IR filter between sample holder and photomultiplier. Powder KDP sample was used as the reference material and the powder SHG efficiency of materials decided from the intensity observed in figure. Intensity for BZOB is more than KDP and for Nd doped BZOB materials greater than BZOB.

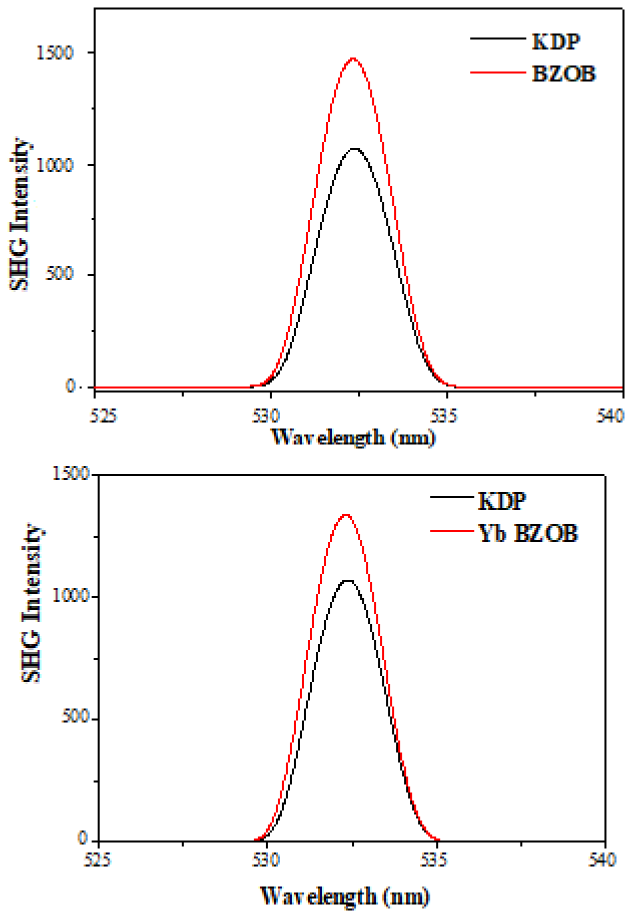

Figure 3.15: SHG intensity Plot of Yb BZOB

4. Conclusions

In conclusion, we report growth and characterization of pure, Nd and Yb doped BZBO crystalline powder materials. The structure and single phase has been studied by using XRD analysis. It shows clear crystalline nature of pure, Nd and Yb doped BZBO. There is no change observed in XRD profile of both materials, hence we can conclude that Nd ion easily incorporate in structure by replacing Bi^{3+} ion of BZBO. The SHG study have been perform using Kurtz and Perry powder technique which shows the enhancement in SHG efficiency of BZBO material due to Nd and Yb doping. The improvement in the SHG by Nd and Yb doping may make it potential material for application in self frequency doubling laser devices.

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