Synthesis of β-BaB_2O_4 thin films from a metallorganic precursor

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β-BaB_2O_4 (β-BBO) thin films have been successfully synthesized by the sol–gel method from a BBO precursor solution. A stable BBO precursor solution was prepared from barium metal and boron triethoxide in a mixed solvent of ethanol and 2-ethoxyethanol. The precursor films crystallized into β-BBO on glass (Corning 7059) and fused silica substrates at 550 °C. BBO films on glass (Corning 7059) and fused silica substrates showed a highly (006) preferred orientation. The absorption edge of β-BBO films on fused silica substrates was at <190 nm. The β-BBO films on glass (7059) and fused silica substrates showed second harmonic generation (SHG) of 532 nm light upon irradiation with 1064 nm Nd:YAG laser light. The SH power from the BBO films has been correlated with the fundamental power through the square-law proportionality based on theory.

Barium metaborate (β-BaB_2O_4, β-BBO) belongs to the acentric space group $R3c$ and is a non-linear optical (NLO) material. The crystal lattice of β-BBO is constructed by a layer-step stacking of alternate Ba^{2+} and $(B_3O_6)^{3-}$ rings.[1–3] The β phase is a low-temperature phase, which is known to be transformed into the high-temperature α phase above *ca.* 925 °C. The α phase belongs to the centric space group $R\bar{3}c$[4] and has no NLO properties. The difference between the α (high-temperature) and the β (low-temperature) forms lies in the barium–oxygen coordination.

β-BBO is characterized by many remarkable features, such as large effective second harmonic generation (SHG) coefficients, a wide transparency range, a broad phase-matched region, and a high damage threshold[5,6] and is a useful material for phase matching in the UV region. Flux and Czochralski methods have been used to grow β-BaB_2O_4 single crystals.[7–9] Nucleation of β-BaB_2O_4 from the melt depends upon various factors, such as the thermal history of the melt and the structure and crystallinity of the starting powders.[9,10] Recently, the preparation of oriented thin films of β-BaB_2O_4 has received great attention because of its applications in integrated non-linear optical devices.

The sol–gel process has many advantages, such as high purity of product, low processing temperature, precise composition control, and the formation of epitaxial coating films. Low-temperature crystallization is the key for the synthesis of the low-temperature β phase. Hirano *et al.* synthesized β-BaB_2O_4 powders and films using boron ethoxide and barium alkoxide.[11,12] However, the films were prepared on non-transparent substrates of Pt. The SHG efficiency of the films crystallized on Pt(111)/glass substrates was measured by the reflection method.[12]

This paper describes the synthesis of highly oriented β-BaB_2O_4 films on transparent glass substrates. β-BaB_2O_4 thin films with preferred orientation were successfully synthesized at 550 °C on glass (Corning 7059) and fused silica substrates from metal alkoxides. The c-axis oriented β-BaB_2O_4 films exhibited frequency doubling of Nd : YAG laser light.

Experimental

Ethanol was dried over magnesium ethoxide and distilled before use. 2-Ethoxyethanol (ethylene glycol monoethyl ether, EGMEE) was dried with molecular sieves and distilled before use. Barium metal and boron triethoxide were commercially available. All procedures were carried out in a dry nitrogen atmosphere. Metal chips of barium were added in portions to an ethanol–EGMEE mixture, and then refluxed producing a barium alkoxide solution. Boron triethoxide in ethanol was added to the solution. The mixed solution was refluxed for 20 h to yield a clear and homogeneous solution. The solution was condensed to about 0.1 mol l^{-1} by removal of solvent at *ca.* 80 °C.

Films were fabricated from the precursor solution by dip coating on glass (Corning 7059) and fused silica substrates. Dip coating on substrates was carried out by dipping a substrate in the precursor solution and withdrawing at a fixed speed of 1.5 mm s^{-1} followed by drying in dry N_2 for several minutes. The precursor films were calcined at 350 °C for 1 h in a water–oxygen gas mixture [oxygen bubbled through water kept at 54 °C ($P_{H_2O}=112$ mmHg)]. The calcined films were placed in a preheated furnace at a desired temperature and heat-treated at that temperature for 1 h in dry flowing oxygen. This procedure was repeated several times to increase the film thickness. The crystallized film thickness per dip coating was *ca.* 0.05 µm.

Crystallized films were characterized by X-ray diffraction analysis (XRD) using Cu-Kα radiation with a monochromator and a pole figure attachment. The film was observed by scanning electron microscopy (SEM). The films were also analysed by transmission electron microscopy (TEM). The BBO films on glass substrates were exposed to 1064 nm light from Nd^{3+} : YAG laser with a pulse duration of *ca.* 8 ns to investigate the second harmonic generation (SHG) effect. The maximum peak power of laser light irradiated on the films was *ca.* 130 kW. The transmitted light from the specimen was filtered, and analysed by a spectrometer with a photomultiplier and a boxcar integrator as shown in Fig. 1.

Results and Discussion

Synthesis of the BBO precursor

The precursor solution synthesized from barium and boron ethoxide in absolute ethanol was slightly unstable and inhomogeneous; however, using 2-ethoxyethanol (EGMEE) as an additive yielded a homogeneous precursor solution for BBO.

The ^{13}C NMR spectra of the BBO precursors synthesized from ethanol–EGMEE (10 : 1) and ethanol–EGMEE (20 : 1) are shown in Fig. 2. The spectra shown in Fig. 2 contain free EGMEE while signals at δ 72.2, 66.2, 60.1 and 15.0 are assigned to carbons of 2-ethoxyethoxy groups bonded to boron. The

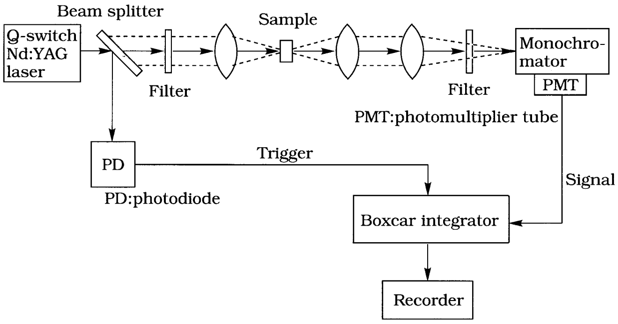

Fig. 1 Experimental setup for the SHG measurement of β-BBO films on glass and fused silica substrates

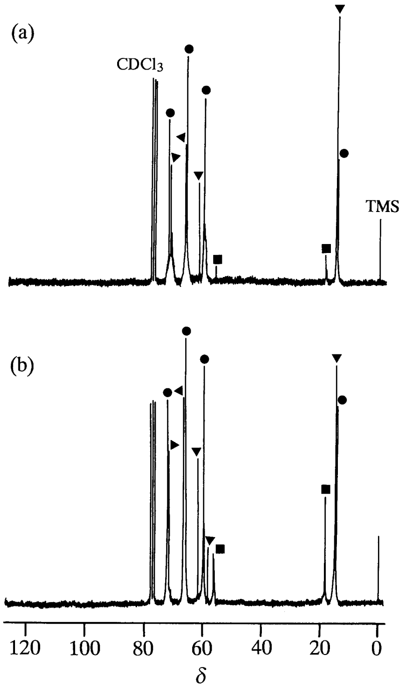

Fig. 2 ^{13}C NMR spectra of the BBO precursors synthesized from (a) ethanol–EGMEE (10:1), (b) ethanol–EGMEE (20:1). ■, Ethoxy group; ●, 2-ethoxyethoxy group; ▼, solvent

downfield shift of the methylene carbon $OCH_2CH_2OCH_2CH_3$ at δ 72.2 indicates the formation of $B-OCH_2CH_2OCH_2CH_3$. The methylene ($HOCH_2CH_3$) and methyl ($HOCH_2CH_3$) carbons of free ethanol appear usually at δ 58.0 and 18.2, respectively. The observed chemical shifts of δ 56.2 and 18.5 in Fig. 2(a) and (b) are assigned to $B-OCH_2CH_3$ and $B-OCH_2CH_3$, respectively.

Therefore, both 2-ethoxyethoxy and ethoxy groups are bonded to boron, when the BBO precursor is synthesized from EtOH–EGMEE. Upon increasing the EtOH content in the mixed solvent from 10:1 [Fig. 2(a)] to 20:1 [Fig. 2(b)], the signals of $MOCH_2CH_3$ increase in intensity. When a large amount of EGMEE is used (10:1), the amount of ethoxy groups attached to the BBO precursor is reduced compared to the system containing less EGMEE (20:1). Using pure EGMEE all ethoxy groups were substituted by 2-ethoxyethoxy groups in the BBO precursor. The coordination ability of the 2-ethoxyethoxy group towards metals is stronger than that of the ethoxy group. Therefore, the amount of coordinated 2-ethoxy groups increases with increasing EGMEE content in the ethanol–EGMEE mixed solvent. The stability of the BBO precursor solution was substantially enhanced by coordination of 2-ethoxyethoxy groups.

The BBO precursor derived from pure EGMEE showed poor wettability to the substrates but this was much improved by using an ethanol–EGMEE mixed solvent. Also, the film quality formed from the mixed solvent system was superior to that from pure EGMEE. This is attributed to the higher thermal stability of $B-OCH_2CH_2OCH_2CH_3$ over $B-OCH_2CH_3$, the organic groups being retained at higher temperature in the pure EGMEE system. Since the BBO precursor using the 10:1 mixed solvent had a better long-term stability than that from the 20:1 system, the former was selected for further study.

Synthesis of BBO thin films

Synthesis of BBO films on glass substrates

The precursor films from the ethanol–EGMEE (10:1) system were crystallized at various temperatures on glass (7059) substrates. When the precursor films were calcined at 380 °C for 1 h in a gas mixture of water and oxygen prior to crystallization, crystalline β-BBO films were formed after heat treatment even at 500 °C for 1 h. Without calcination, however, no crystalline film was obtained at 500 °C on these substrates. Water vapour can effectively remove organic residues during calcination, as reported in the low-temperature synthesis of $LiNbO_3$ powders.[13] Also, water vapour promotes condensation reactions of the coordinated alkoxy groups in the precursors, leading to low-temperature crystallization of oriented BBO on glass substrates. The low crystallization temperature has an advantage for the prevention of reaction between films and substrates. Also, low crystallization temperature is required to avoid grain growth, which results in the formation of cloudy films.

Although crystalline BBO films began to form at 500 °C, a temperature of 550 °C was selected in order to increase the film crystallinity whilst it was still low enough to prevent reaction between films and substrates as well as grain growth. Fig. 3 shows XRD profiles of BBO films crystallized at 550 °C on glass (7059) and fused silica substrates. Each film shows a strong 006 reflection accompanied by a 104 reflection. The (006) plane orientation of the film on glass substrates is the same as found on Pt substrates.[11,12]

The (006) preferred orientation of BBO film was further analysed by X-ray pole figure measurements. The X-ray pole figure constructed for the (200) plane showed no spot pattern but only diffuse rings. Therefore, the film shows only a (006)

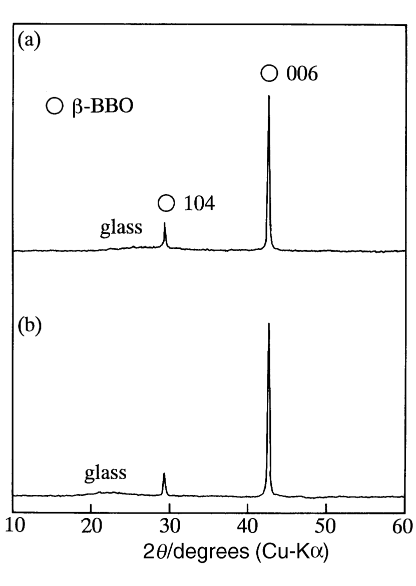

Fig. 3 XRD profiles of BBO thin films on glass substrates crystallized at 550 °C for 1 h. (a) Glass (7059) substrate, (b) fused silica substrate.

preferred orientation with in-plane rotation, and no three-dimensional regularity perpendicular to the substrate.

Since both glass (7059) and fused silica substrates are amorphous, and have no specified crystallographic plane, the (006) plane of β-BBO is one of the most easily developed planes on substrates. The anionic $(B_3O_6)^{3-}$ group in β-BBO is nearly planar with its plane perpendicular to the three-fold axis which passes through the centre of the ring. The planar ring anion $(B_3O_6)^{3-}$ is parallel to the (006) plane of the unit cell of β-BBO. Thus the (006) orientation is generally observed on glass and fused silica substrates.

The β-BBO thin films on the fused silica substrates were highly transparent. Fig. 4 shows the transmittance of a β-BBO thin film on a fused silica substrate. The absorption edge of fused silica itself is at 180 nm while the absorption edge of the film is below 190 nm, in good agreement with that reported for a single crystal.[6]

An edge-on SEM photomicrograph of a BBO film on a fused silica substrate is shown in Fig. 5. The film shows a smooth surface with no cracks or voids. The film thickness is *ca.* 1.0 µm after 20 dippings. The BBO films on glass (7059) substrates were found to have similar film qualities as observed by SEM.

Fig. 6 shows a cross-sectional TEM photograph of a BBO thin film crystallized at 550 °C on a fused silica substrate. The clear interface between the BBO film and the fused silica substrate indicates the absence of interdiffusion or reaction at the interface. The SAD pattern is in good agreement with that of β-BBO. The ring profile of SAD shown in Fig. 6 exhibits in-plane rotation of BBO crystallites, although the film has a preferred orientation along the (006) plane, consistent with the result of X-ray pole figure measurements.

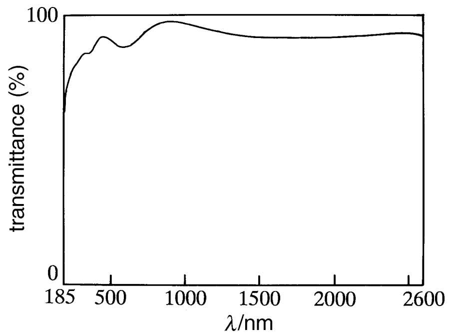

Fig. 4 Transmittance of BBO thin film crystallized at 550 °C on a fused silica substrate

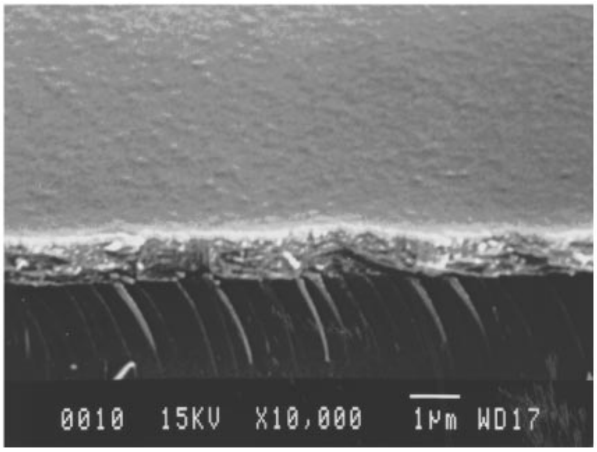

Fig. 5 Edge-on SEM photograph of a fractured BBO film crystallized at 550 °C for 1 h on a fused silica substrate

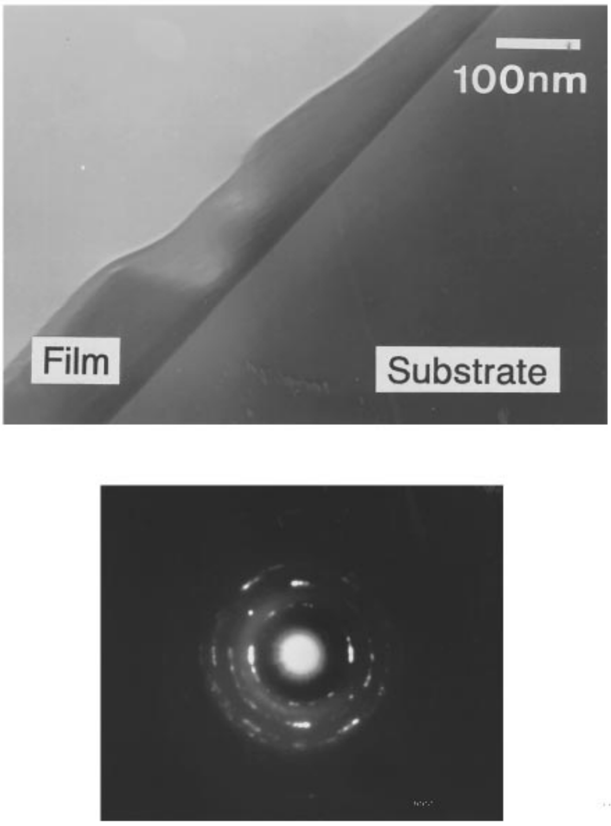

Fig. 6 Microstructure (upper) and selected area electron diffraction pattern (lower) of a BBO thin film on a fused silica substrate

Second harmonic generation (SHG) of BBO thin films

The SHG effect was analysed for β-BBO thin films crystallized on glass and fused silica substrates at 550 °C. The films were irradiated with the fundamental laser wavelength of 1064 nm and transmitted light through the β-BBO film was found to include 532 nm light. Fig. 7 shows the relation between the incident light power and the transmitted light (SH wave) power from 1.0 µm β-BBO films on glass (7059) and fused silica substrates and the SH power from each film was found to be comparable. β-BBO films on glass and fused silica substrates showed slopes of 1.90 and 2.06, respectively, in Fig. 7; so

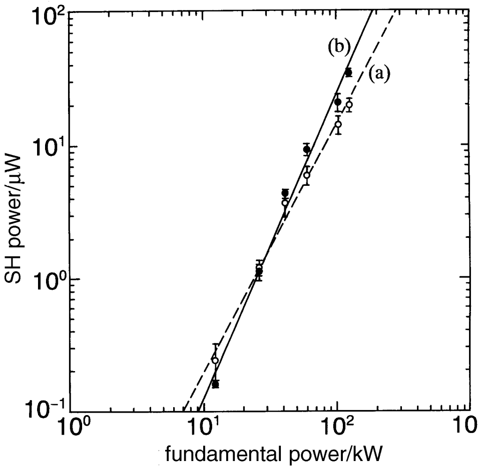

Fig. 7 Power relationship between the fundamental light (1064 nm) and second harmonic light (532 nm) for β-BBO thin films on transparent substrates crystallized at 550 °C: (a) film on a glass substrate, (b) film on a fused silica substrate

Table 1 SHG efficiency of β-BBO thin films on fused silica and glass (7059) substrates

substrate	film thickness, t/μm	SHG efficiency η	(η/t^2)/μm^{-2}
fused silica	2.0	2.4×10^{-10}	6.0×10^{-11}
glass(7059)	2.0	1.6×10^{-10}	4.0×10^{-11}
glass(7059)	2.6	3.1×10^{-10}	4.6×10^{-11}

satisfying the square-law proportionality between the fundamental power (P_ω) and the harmonic power ($P_{2\omega}$).

Table 1 summarizes the SHG efficiencies (η) of β-BBO thin films on glass (7059) substrates. Since the film thickness is sufficiently small compared to the coherence length of bulk BBO ($l_c = 15$ μm),[5] the intensity of the SHG wave is proportional to the square of the film thickness (t^2).[14] Thus, the value of η/t^2 is similar for both 2.0 and 2.6 μm films. The efficiencies of the films are lower than those of single crystals, since the phase match condition is not satisfied.

Conclusions

β-BBO films with c-axis preferred orientation have been synthesized from a BBO precursor solution at 550 °C on glass and fused silica substrates. The films were highly transparent and showed an absorption edge at 190 nm as well as displaying second harmonic generation.

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