Enhanced Nonlinear Thin Films of *β*-Barium Borate by Sol−Gel Synthesis

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β-Barium borate (*β*-BaB_2O_4; *β*-BBO) thin films with a dominant (104) orientation were fabricated for the first time by the addition of urea during a sol−gel synthesis. The bonding between urea and Ba appears to effectively reduce the internal stresses within the material, leading to crack-free, mirror-like films. The quality of the films is strongly dependent on the refluxing time and the urea/barium molar ratio. It is believed that urea acts as a seed for film growth in the (104) direction instead of the usual (006) orientation. The reoriented thin films exhibit an unprecedented enhanced nonlinear efficiency which is approximately five times that obtained using (006) oriented samples.

Introduction

Beta-barium borate (*β*-BaB_2O_4, *β*-BBO) is a well-known nonlinear optical material with a large second-order nonlinear susceptibility ($\chi^{(2)} = 2.2$ pm/V), a wide transparency range (189−3500 nm), and a high damage threshold.[1,2] Single *β*-BBO crystals are commonly incorporated into commercial laser systems as components for frequency doubling or tripling, and as the main nonlinear element in optical parametric oscillators (OPO) pumped by a UV laser.[3] The nonlinear efficiency of a crystal is determined by its crystallinity, orientation, and phase-matching.[4,5]

Thin films of *β*-BBO have also been proposed as key nonlinear elements in compact optical systems such as frequency converters, waveguides, and switches.[6,7] A variety of methods have been used to fabricate (006) *β*-BBO thin films whose *c*-axis lies normal to the substrate.[8–17] As shown in Figure 1a the (006) orientation corresponds to the situation when the $(B_3O_6)^{3-}$ anionic rings lie parallel to the substrate. This orientation is energetically favorable as the $(B_3O_6)^{3-}$ rings can adjust themselves to decrease the interfacial energy with the substrate.[12] The Ba^{2+} counterions (not shown in Figure 1a) lie between the rings. From a nonlinear optical perspective, however, bulk crystals have their best efficiencies at a noncollinear angle θ relative to the optical axis due to enhanced phase matching.[18] Thin films with a tilted *c*-axis with respect to the substrate are also expected to be more advantageous for waveguide application involving second harmonic generation.[1,2] To date however there have been no published reports on *β*-BBO thin film fabricated with any other orientations that exhibit a high nonlinear response other than (006).

A schematic illustration of the crystal structure plane corresponding to the (104) orientation ($d = 3.05$ Å, $2\theta = 34.16°$ for a Co target at $\lambda = 1.792$Å) in *β*-BBO is shown in Figure 1b. The (104) orientation determined by the interactions between the Ba^{2+} ions and the $(B_3O_6)^{3-}$ anionic rings is also an easily developed crystallographic feature[19,20] and, in other reported X-ray diffraction (XRD) spectra,[8–17] always accompanies the (006) plane, albeit, with a much lower intensity. Figure 1 shows that while the (006) plane is parallel to the $(B_3O_6)^{3-}$ rings there is a ~14° tilt angle between the (006) and (104) planes. This tilted orientation most likely corresponds to a direction where the internal stresses are higher. Indeed, when Kobayashi et al. [11] analyzed

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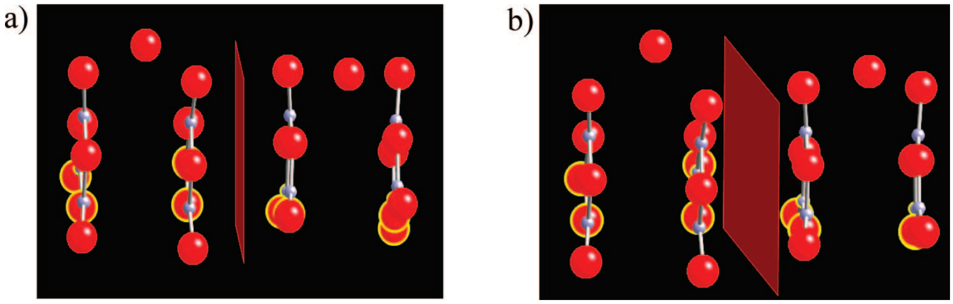


Figure 1. Side view of the β-BBO unit cell. The red balls represent O atoms while the small gray balls represent B atoms. The Ba atoms are not shown. The red plane shows the defined plane orientation for the (a) (006) plane and (b) (104) plane.

their β-BBO thin films by XRD spectroscopy, they found that the (104) orientation existed mainly at the crack boundaries of the material. This may explain why β-BBO exhibits a preferred (006) orientation but also why the (104) plane can be detected.

One strategy which can be used to change the growth orientation of β-BBO is to use a molecular seed that can promote thin film growth in the desired direction by reducing the internal stresses in the crystal until they are less than those associated with a film oriented at (006).

In this paper, thin films of β-BBO have been fabricated by a new modified sol−gel synthesis involving an additive, urea, $(NH_2)_2CO$, which is found to promote crystal plane growth along the (104) direction. This resultant films exhibit a much larger nonlinear efficiency for second harmonic generation than those having a (006) orientation.

Experimental Section

The sol−gel synthesis to make β-BBO uses boron ethoxide and metal barium, Ba, as starting materials. The Ba ethoxide ($Ba(OEt)_2$) solution, obtained by dissolving metallic Ba in anhydrous ethanol, was mixed with boron ethoxide in a molar ratio of 1:2. This solution mixture was subsequently added to a solvent mixture of ethanol and 2-ethoxyethanol ($2\text{-}C_2H_5O{-}C_2H_5OH$) to make a ∼0.2 mol/L precursor solution.

Urea powder was then added to the solution, with differing urea:Ba (UB) molar ratios ranging from 1:8 to 3:1. The thin films obtained from these different solutions are labeled UBx where x is the value of the urea:Ba mole ratio. After the urea was completely dissolved, the solution was refluxed at ∼70 °C for 16 h until it was colorless and homogeneous. Refluxing at temperature higher than 80 °C resulted in a precipitate which arises from the decomposition of urea and the subsequent formation of insoluble $BaCO_3$.

Films were fabricated by depositing ∼1 or 2 drops of precursor solution onto a fused silica substrate (∼1 × 1 cm^2) and spin coating at 1000 rpm. After drying in air, the films were heat treated as follows at ambient pressure. First, the film was heated for 30 min at a predefined low temperature between 150 to 250 °C in an oven filled with water vapor to hydrolyze the material. The temperature was then raised to 650 °C for 1 h to form the β-BBO phase.

The solutions were examined by ultraviolet (UV)−visible spectroscopy while the films were characterized by a number of techniques including power XRD using a Co source (λ = 1.792 Å) and scanning electron microscopy (SEM).

Results and Discussion

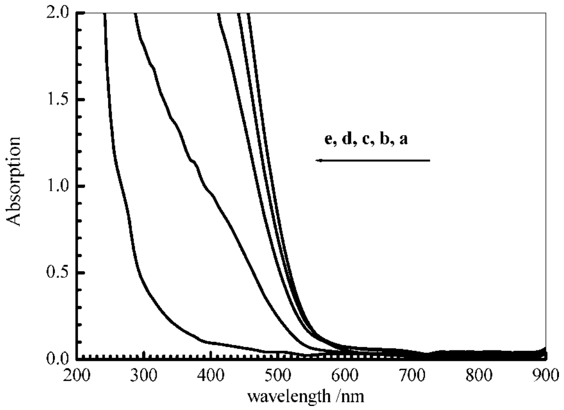
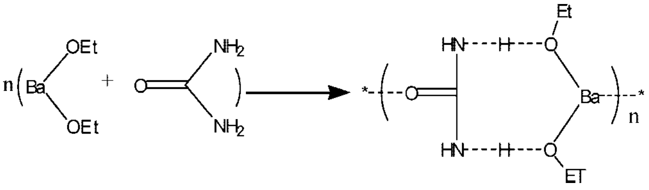


Figure 2. UV−visible spectra of BBO precursor solutions with different urea:Ba (UB) mole ratios. a, UB0; b, UB0.25; c, UB0.5; d, UB0.75; e, UB1.

Without the addition of urea the precursor solutions were an orange or reddish color which becomes deeper with increased refluxing times or temperatures. The absorbing species is attributed to a Ba impurity because the same absorption spectrum was found when metallic Ba was dissolved alone in water or alcohol. The wavelengths of the impurity absorption band lies below 550 nm (Figure 2) which limits the frequency doubling efficiency of the resultant thin films in the visible region of the spectrum. Figure 2 also shows that increasing the urea doping concentration effectively suppresses the formation of the impurity. The solutions ultimately become colorless when the UB mole ratio reaches unity. As shown below the thin films obtained from the colorless solution exhibit an enhanced nonlinear efficiency.

It is postulated that formation of the Ba impurity is suppressed by the following reaction between urea and Ba ethoxide:



Here, the Ba precursor is stabilized by hydrogen bonding between the amine groups of urea and the oxygen atoms in $Ba(OEt)_2$. When the UB doping ratio is <1, however, the excess Ba can still generate the impurity compound, which leads to a colored solution.

The β-BBO phase formed at 650 °C using precursor solutions doped with urea, just as it did using solutions

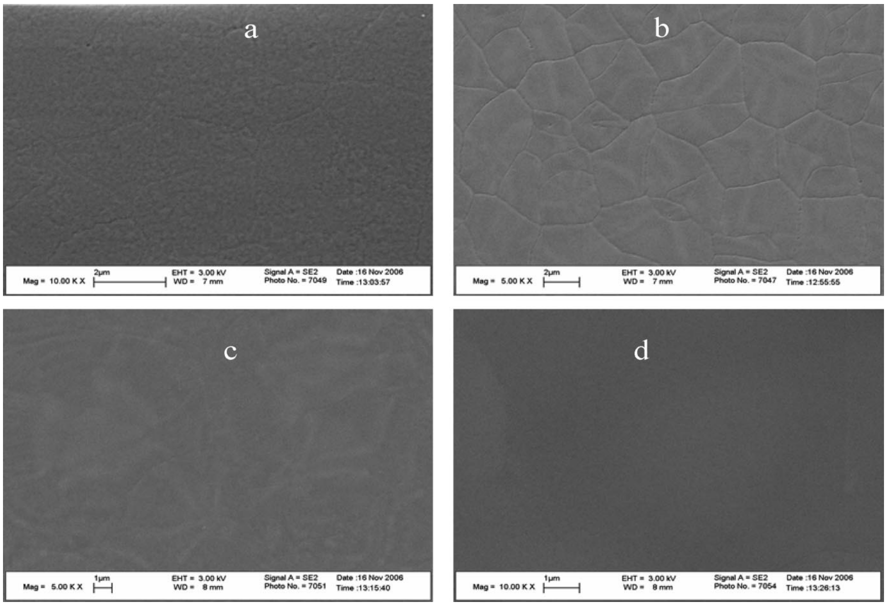


Figure 3. SEM images of thin films formed by hydrolysis at 150 °C and then heated to 650 °C for 1 h to form the β-BBO phase. The precursor solution UB1 was refluxed at 70 °C for different times: (a) 0 h; (b) 1 h; (c) 4 h; and (d) 16 h.

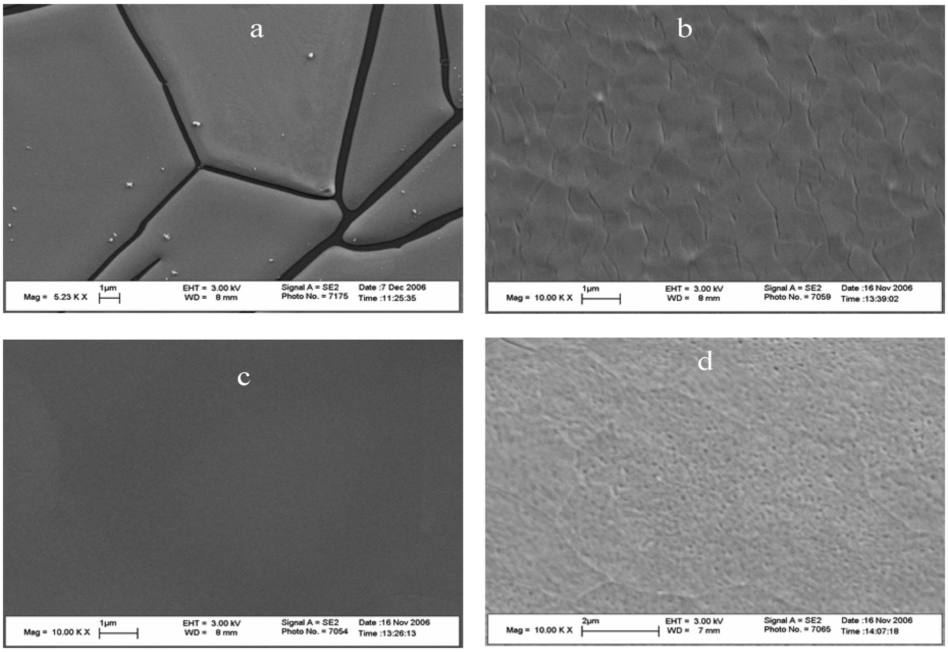


Figure 4. SEM images of thin films made from different precursor solutions. (a) A UB0 film; (b) a UB0.5 film; (c) a UB1 film; and (d) a UB2 film. All films were hydrolyzed at 150 °C for 30 min and then heated to 650 °C for 1 h to form the β-BBO phase.

without urea. [8,20] However, in the former case it was found to be necessary to slowly increase the temperature to 650 °C at a rate of 10 °C/min in a fresh dry air or O_2 environment to avoid the production of CO_2 gas during the calcination process.

The UB1 films (~100 nm) are slightly thicker than samples made without urea (~80 nm), probably because the solution viscosity is enhanced by the addition of urea.[8] The films formed with a urea additive adhere strongly to the substrate, and thicker films could be obtained by multiple coatings.

The precursor solution refluxing time had a large effect on the morphology of the thin films. To make meaningful comparisons, only the UB1 precursor solution refluxing time was varied while the spin-coated samples were subjected to the same heat treatment: 150 °C hydrolyzation for 30 min followed by crystallization at 650 °C for 1 h.

UB1 β-BBO thin films produced from a solution that was not refluxed exhibit irregular and random defects (Figure 3a). After 1 h of refluxing, the resultant films were cracked with grain sizes of ~2−4 μm in dimension (Figure 3b). However, the cracks began to disappear when the refluxing time was increased to 4 h (Figure 3c) and then completely disappeared after 16 h of refluxing, yielding mirror-like films (Figure 3d).

Kobayashi et al.[11] suggested that the cracks formed in the β-BBO thin films are due to lateral internal stresses that arise after the film adheres to the substrate. In our work, since the cracks are reduced with increased refluxing time, it can

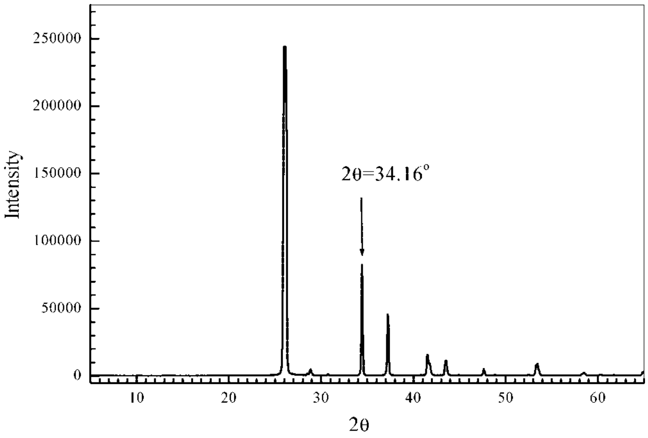


Figure 5. Measured XRD spectra of urea powder used in the experiment.

be concluded that an increased refluxing time allows the reaction between urea and Ba ethoxide to proceed to completion and that the product of the reaction relaxes the stresses within the material. Without refluxing the urea will not react with the Ba ethoxide fast enough before it simply evaporates from solution. As a result, β-BBO thin films are poorly formed and have random defects throughout. When the urea−Ba ethoxide reaction is allowed to go to completion, the resultant thin films exhibit minimal light scattering losses and have an improved nonlinear response.

Figure 4 shows SEM images of the β-BBO films as a function of the urea doping concentration. Without urea doping, the UB0 film has a cracked mosaic structure[8] (Figure 4a). The cracks begin to disappear as the UB mole ratio is increased to 0.5 (Figure 4b) and are completely absent for a UB1 sample. Increasing UB to 2, however, has a detrimental affect on the film morphology (Figure 4d). It is thought that void regions are formed when the excess urea decomposes and evaporates out of the film.

An XRD spectrum of urea powder used in the experiment is shown in Figure 5. One diffraction peak at $2\theta = 34.16°$ corresponding to (111) plane ($d = 3.05$ Å) of urea (space group $P\bar{4}21m$)[21,22] exactly matches with the d-value of the (104) plane of a β-BBO crystal. The XRD spectrum of a freshly spin-coated precursor film, measured within 1 h of preparation, also shows a small peak at $2\theta = 34.16°$ (Figure 6a). However, this feature disappears after 1 day at ambient conditions presumably due to the evaporation of urea (Figure 6b). Indeed, β-BBO films with a preferred (104) orientation could only be fabricated using freshly coated precursor solutions, while (006) films were formed from spin coated samples allowed to sit in air. This shows that the presence of urea is critical for growing β-BBO thin films with the (104) crystal structure.

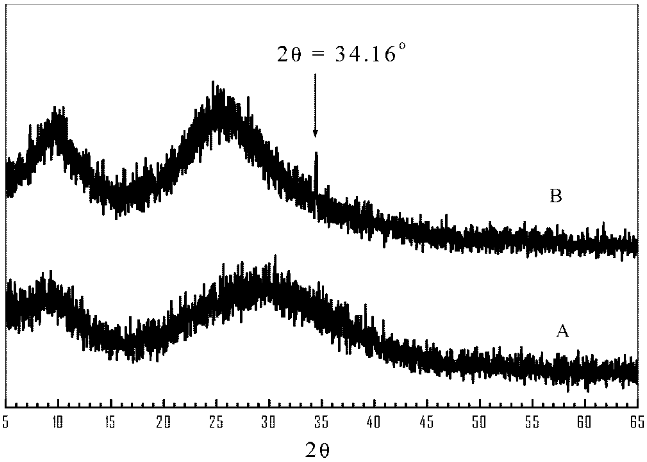


Figure 6. XRD spectra of UB 1 precursor films. A: A sample measured 1 day after spin-coating. B: A sample measured within 1 h after spin-coating.

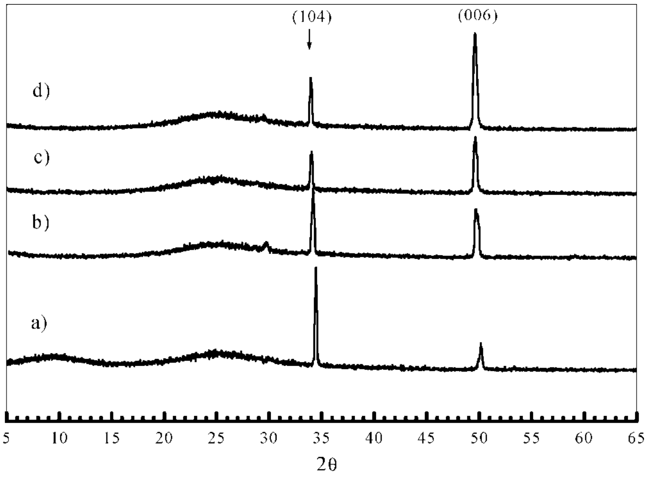


Figure 7. XRD spectra of UB1 films formed at different preheating temperatures: (a) 150 °C; (b) 175 °C; (c) 200 °C; and (d) 250 °C.

The first preheat treatment is also critical for controlling the (104) orientation of β-BBO thin films made from a UB1 precursor. As shown in the XRD spectra in Figure 7, when the hydrolyzation temperature is ~150 °C, the (104) signal is much stronger than the (006) peak at $2\theta = 50°$, with an orientational degree of ~80%. The very slight peak position shift (within ±0.2°) is an experimental effect due to the use of two different thin film holders with different thicknesses during the measurements. As the treatment temperature is increased, the (006) and (104) signals become comparable, and then eventually, the (006) begins to dominate.

The hydrolyzation temperature of 150 °C lies close to the melting point of urea (133 °C),[23] and therefore, equilibrium is probably established between the urea solid and gas phases. This temperature allows enough urea to act as a seed for β-BBO growth along the (104) direction. However, at higher temperatures it is difficult for urea crystallites to act as a seed as they would most likely evaporate too quickly from the film. As shown in the Figure 7 when this happens, a (006) orientation dominates as if the urea had not been added at all.

The XRD spectra in Figure 8 show that the β-BBO thin film orientation shifts from (006) to (104) as the urea concentration is increased. The (104) plane dominates the

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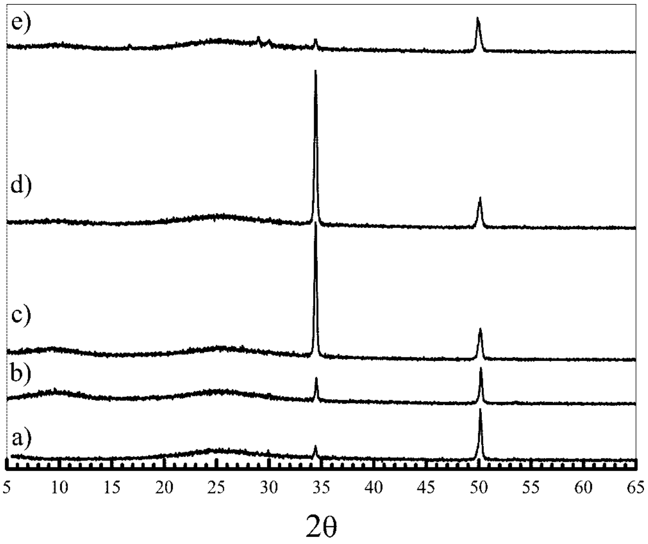

Figure 8. XRD spectra of β-BBO thin films formed using different urea doping concentrations. (a) A UB0 thin film; (b) a UB0.5 thin film; (c) a UB1 thin film; (d) a UB2 thin film; and (e) a UB3 thin film.

UB1 and UB2 samples with a degree of crystallinity > 80%. However, the dramatic change in the XRD spectrum of a UB3 film shows that this sample is polycrystalline. The intensity of the (104) peak in the XRD spectrum of the UB1 sample is much higher than the intensity of the (006) feature found for UB0. The reasons for this are the same as those presented above: the presence of urea not only inhibits the generation of Ba impurities and releases the internal stress during the film formation, it also promotes the (104) orientation during crystallization due to the seeding effect. However, again, the evaporation of excess urea from the higher UB ratio sample (UB3) results in defects that dramatically reduce the degree of crystallinity of the thin film (Figure 4d). It is worth noting that (006) orientation is always observed in all samples because aligning the *c*-axis of the β-BBO crystal perpendicular to the substrate is the most energetically favorable configuration.

The quality of the films was assessed by measuring second harmonic generation (SHG) signals obtained by irradiating the samples with the 1064 nm infrared output of a Nd:YAG laser (Spectra-Physics Pro-250, 20 Hz repetition rate, 4 ns/pulse). As described previously,[8] the SHG signal was dispersed from the fundamental beam using a monochromator, detected with a photomultiplier, and monitored on a digital oscilloscope (Tektronix, TDS744A). The β-BBO SHG responses detected by the oscilloscope are shown in Figure 9. The SHG intensity strongly correlates with the thin film orientation. The nonlinear response of the (104) film (100 nm thick) is found to be more than 5 times larger than that found for the (006) film (80 nm thick) for the same fundamental laser input power. The magnitudes of the effective second-order nonlinear coefficients, d_{eff}, of the (104) and (006) films were measured relative to a reference Y-cut quartz crystal plate and found to be 3.8 ± 0.5 pm/V and 1.7 ± 0.1 pm/V,[8] respectively. The latter value is comparable to the results obtained from other reports,[12,13,15,16] which indicates that the maximum d_{eff} corresponds closely to the d_{22} value for bulk crystalline β-BBO = 2.2 pm/V.[1] The *d*-value for the (006) thin film is reasonable given that the microstructure of the thin film is expected to scatter the laser light and that the presence of absorbing Ba impurities will decrease the nonlinear optical efficiency. The enhancement of the nonlinear efficiency observed for the (104) films is unprecedented, surpassing the d_{eff} of films made with a (006) orientation. In light of the small thickness of the films made in this work, this enhancement is not due to a phase-matching effect.[20] Instead, it suggests that the second-order nonlinear susceptibility of β-BBO grown with a predominant (104) orientation is larger. These samples are still under investigation and will be the subject of a later publication.

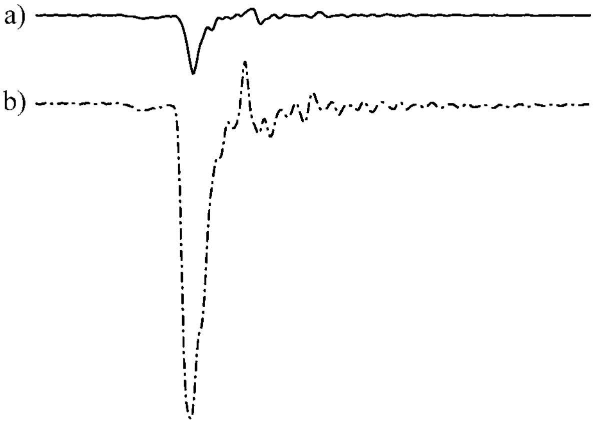

Figure 9. Oscilloscope traces of the SHG response of β-BBO thin films with (a) a preferred (006) orientation and (b) a preferred (104) orientation.

Conclusions

The addition of urea to the sol−gel precursor solution has been found to have a dramatic and positive effect on the morphology and nonlinear efficiency of the β-BBO thin films formed by spin-coating. The urea appears to bond with the Ba ethoxide precursor and reduce the internal stress of the film as it forms. This leads to flat and highly transparent thin films. XRD spectra show that the *c*-axis of the films is tilted with respect to the substrate and has a predominately (104) orientation. The reason for this is that urea has a crystal plane which perfectly matches the (104) orientation of β-BBO and, therefore, can act as a seed for growth in this direction.

These films are expected to find wide use in photonic devices and as doublers for ultrashort laser pulses. It is also believed that this method can be extended to the fabrication of other thin films with desired orientations given that an appropriate seed can be found.

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