Synthesis and characterization of beta barium borate thin films obtained from the BaO–B₂O₃–TiO₂ ternary system


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Abstract

This work reports on the synthesis and the structural and optical characterization of beta barium borate (β-BBO) thin films containing 4, 8 and 16 mol% of titanium oxide (TiO₂) deposited on fused silica and silicon (0 0 1) substrates using the polymeric precursor method. The thin films were characterized by X-ray diffraction, Raman spectroscopy, atomic force microscopy and scanning electron microscopy techniques. The optical transmission spectra of the thin films were measured over a wavelength range of 800–200 nm. A decrease was observed in the band gap energy as the TiO content was raised to 16 mol%. Only the β-BBO phase with a preferential orientation in the (0 0 1) direction was obtained in the sample containing 4 mol% of TiO₂ and crystallized at 650 °C for 2 h.

Keywords: Beta barium borate; Thin films; Polymeric precursor method; BaO–B₂O₃–TiO₂

1. Introduction

The low temperature beta barium borate phase (β-BaB₂O₄, or so-called β-BBO) possesses interesting optical properties such as a large second harmonic generation (SHG) coefficient, a wide range of transparency, a broad phase-matched region and a high damage threshold [1,2]. Thin films of β-BBO phase can be applied in optical devices such as frequency converters, waveguides and switches [3,4]. These applications have led to increasing interest in the development of new techniques to produce thin films of the β-BBO phase.

Several methods have been applied to obtain β-BBO phase in thin film form [4–11]. A β-BBO thin film displaying a (0 0 1) preferred orientation was obtained by chemical solution deposition techniques [5–7,11], pulsed laser deposition (PLD) [8], magnetron sputtering [9] and metalorganic chemical vapor deposition (MOCVD) [4,10]. Each of these methods has advantages and disadvantages. Physical methods such as PLD or magnetron sputtering are usually considered very expensive compared to chemical methods. On the other hand, the preparation of these thin films by some chemical methods such as sol–gel and MOCVD requires the use of complex and sometimes very costly materials used as precursors for the production of thin film.

A new approach for the chemical synthesis of thin films, based on a method developed by Pechini [12], has been extensively used to produce a large variety of materials [12,13]. This method is based on chelating or complexing of cations by a hydrocarboxylic acid such as citric acid [12]. Compared to other chemical methods, the polymeric precursor method, or Pechini’s method, offers the advantage of using common reagents and does not require a special atmosphere.

In the last decade, glass–ceramic materials containing the β-BBO phase were obtained from the crystallization of the BaO–B₂O₃–TiO₂ vitreous system [14,15]. According to these reports, the difficulty of obtaining the β-BBO phase from the 50BaO–50B₂O₃ stoichiometric composition was overcome by the addition of titanium oxide (TiO₂) compound in the BaO–B₂O₃ system. Although the vitreous phase contained a large quantity of TiO₂ (up to 16% in mol%), it was possible...
to obtain the β-BBO as the major phase when the glassy phase was subjected to an isothermal crystallization process [14,15].

Based on these trends, this paper reports on the synthesis and characterization of β-BBO thin films obtained from the BaO–B₂O₃–TiO₂ system, using the modified Pechini method. Different compositions containing 4, 8 and 16 mol% of TiO₂ were synthesized and characterized by X-ray diffraction (XRD), Raman spectroscopy, atomic force microscopy (AFM) and scanning electron microscopy techniques. The optical-absorption properties of the thin films were measured. The effect of different substrates and the effect of the TiO₂ content on the synthesis of the β-BBO phase were analyzed.

2. Experimental details

Precursor solutions were prepared by the polymeric precursor method (modified Pechini method) [12]. Barium citrate was formed by dissolving barium carbonate (99.7% purity) in an aqueous solution of citric acid (70–80 °C). After homogenizing the Ba-citrate solution, a stoichiometric amount of titanium isopropoxide (98% purity) was added to the Ba-citrate solution in accordance with the three aforementioned compositions. The three compositions studied were named: BBO:4%TiO₂ (48BaO–48B₂O₃–4TiO₂), BBO:8%TiO₂ (46BaO–46B₂O₃–8TiO₂) and BBO:16%TiO₂ (42BaO–42B₂O₃–16TiO₂) (in mol%). The solutions were stirred slowly for approximately 3 h and their pH adjusted to 2–3, using NH₄OH. After homogenization of the solutions containing the Ba and Ti cations, sorbitol (99.6% purity) and H₃BO₃ (99.8% purity) were dissolved in water and added to the citrate solutions. Sorbitol was added to promote mixed citrate polymerization by a polyestefi-

racion reaction. The molar ratio of citric acid and the metal was 3:1; the citric acid/sorbitol ratio was set at 60:40 (mass ratio). To increase the thickness of the thin films, five depositions were made on fused silica and silicon (0 0 1) substrates by spin-coating. After each deposition, the film was dried at 100 °C for 20 min. After intermediary annealing at 400 °C for 2 h under a 1 °C/min heating-rate, the thin films were annealed at 650 °C/2 h in an O₂ atmosphere. This procedure was repeated for each layer.

The crystallographic structure of the thin films was analyzed using a Rigaku Dmax 2500PC X-ray diffractometer with Cu Kα radiation (50 kV/100 mA, 1.5405 Å) in a θ–2θ configuration using a graphite monochromator. An angular range (2θ) from 20 to 60°, a step of 0.02° and a scanning rate of 2°/min were applied. Raman spectra were registered at room temperature using a micro-Raman Renishaw R2000 system. The samples were excited with a 632.8 nm He–Ne line and the Raman spectra collected between 300 and 1800/cm with a spectral resolution of approximately 1/cm. The thickness of the thin films was measured by scanning electron microscopy (Zeiss, DSM 940) cross-section while an AFM (Digital Instruments Multimode Nano-
scope IIIa) was used to measure the surface roughness and surface grain size, taken at room temperature using contact mode. The optical transmittance of thin films was measured using a Cary-5G UV/Vis double-beam spectrophotometer in a wavelength range of 200–800 nm. The thin films deposited on fused silica substrates were exposed to a 1064 nm beam from a Nd:YAG laser (Spectron Laser Systems, Model SL404G) to investigate the SHG effect. The specimen’s transmission light (532 nm) was analyzed with a photomultiplier (Hamamatsu, Model R910).

3. Results and discussion

3.1. Structural properties

Fig. 1 shows the XRD patterns (θ–2θ scan) of the BBO:4%TiO₂, BBO:8%TiO₂ and BBO:16%TiO₂ thin films deposited by spin-coating on the fused silica and silicon (0 0 1) substrates. The crystallographic planes of the β-BBO phase are identified in the X-ray patterns by the parenthesis placed above their respective diffraction peaks.

The most intense diffraction peak in the BBO:4%TiO₂ thin film deposited on fused silica appeared on the (0 0 6) crystallographic plane of the β-

BBO phase. The other two peaks, less intense, were attributed to the (1 2 2) and (1 0 4) crystallographic planes. The X-ray pattern of BBO:8%TiO₂ thin film revealed two peaks with similar intensities on the (1 2 2) and (1 0 4) planes. The addition of 16 mol% of TiO₂ favored the formation of the BaTiO₃ crystalline phase coexistent with the β-BBO crystalline phase. The ratio among the areas of the main diffraction peaks of the β-

BBO and BaTiO₃ phases observed in the XRD patterns of BBO:16%TiO₂ thin film deposited on fused silica was approximately equal to 0.34.

The BBO:4%TiO₂ thin film deposited on silicon (0 0 1) substrate presented a very intense peak attributed to the (0 0 6) plane of β-BBO phase and a second, less intense peak attributed the (1 0 4) plane of the same phase, indicating that the BBO:4%TiO₂ thin film had a preferred orientation in the (0 0 1) direction. Diffractograms of the thin films containing 8 and 16 mol% of TiO₂ deposited on silicon (0 0 1) substrate showed similar patterns, with diffraction peaks of the β-BBO, BaTiO₃ and Ba₄B₂O₇ crystalline phases.

The degree of preferred orientation in the BBO:4%TiO₂ sample was evaluated based on Lotgering’s method [16], whereby the degree of orientation f is expressed by the following equations:

\[ f = \frac{(P - P_0)}{(1 - P_0)}, \]
\[ P_0 = \frac{I_{0006}}{\sum I_{0(hkl)}} \]  
\[ P = \frac{I_{0006}}{\sum I_{(hkl)}} \]

where \( I_{0006} \) is the (0 0 6) peak intensity and \( \sum I_{0(hkl)} \) is the sum of the intensity of all the peaks appearing in the powder diffraction data of \( \beta \)-BBO phase obtained from the JCPDS file number 80-1489 [17]. \( I_{0006} \) is the (0 0 6) peak intensity and \( \sum I_{(hkl)} \) is the sum of the intensities of all the peaks in the experimental diffraction data of the \( \beta \)-BBO thin films shown in Fig. 1a and b.

The degree of orientation for thin film deposited on fused silica substrate was 0.79 and 0.89 when deposited on the silicon (0 0 1) substrate. These results demonstrate that the (0 0 1) preferred orientation derived not from lattice matching but from other effects. In cases where lattice matching is absent, the planes having a lower interfacial energy are expected to grow preferentially. The interfacial energy decreases as the atomic plane density increases [18]. Therefore, the plane with the highest atomic density tends to grow preferentially, especially in anisotropic films [19,20]. The \( \beta \)-BBO structure is composed of nearly planar (B\(_3\)O\(_6\))\(^{3-} \) rings perpendicular to its polar axis, bonded together by Ba\(^{2+} \) ions [2]. The atomic density of the (0 0 1) plane is higher than all the other crystallographic planes in the \( \beta \)-BBO structure. On the other hand, the interaction between (B\(_3\)O\(_6\))\(^{3-} \) rings and Ba\(^{2+} \) ions is also considered to be strong in the (1 0 4) plane direction [21]. Therefore, the (1 0 4) plane is also easily developed during crystallization.

The BBO:4%TiO\(_2\) thin film deposited on silicon (0 0 1) substrate presented a degree of preferential orientation equal to 0.89 in relation to the \( c \) axis. This value is comparable to that obtained by other methods as, for instance, for thin films obtained by the sol–gel method.

Fig. 1. XRD patterns of thin films with five layers annealed at 650 °C, deposited on (a) fused quartz and (b) silicon (0 0 1) substrates.
method through metal alkoxide, in which a degree of 0.88 was achieved [5].

In short, the addition of 4% of TiO₂ to the BaO–B₂O₃ system promoted the formation and stabilization of thin film with only the β-BBO crystalline phase at a low crystallization temperature (650 °C) and with a high degree of preferred orientation.

Fig. 2 shows the Raman spectra of thin films deposited on silicon (0 0 1) substrate. As can be observed, Raman bands were present in the spectra of all the films containing varying amounts of TiO₂. In agreement with Ney et al. [22], the Raman lines located at 670/cm were attributed to the ν₁₃ vibrational mode of the boron and oxygen atoms outside the (B₂O₃)³⁻ rings of β-BBO crystalline phase. The low intensity of the Raman lines can be explained by the thickness of the thin films (≈335 nm for BBO:4%TiO₂, 229 nm for BBO:8%TiO₂ and 235 nm for BBO:16%TiO₂) and by the existence of a relatively preferential orientation in the (0 0 6), (1 0 4) and (1 2 2) crystallographic directions. No other Raman lines relating to other crystalline phases were observed in the Raman spectra.

3.2. Microstructural properties

Figs. 3 and 4 show the AFM surface images of the BBO:4%TiO₂, BBO:8%TiO₂ and BBO:16%TiO₂ thin films deposited for 2 h on fused silica and silicon (0 0 1) substrates at 650 °C. The roughness and grain size of thin films revealed by the AFM images are given in Table 1. An analysis of the AFM images showed that the type of substrate did not influence the thin films’ microstructure. However, the grain size was found to decrease with increasing amounts of TiO₂. We believe that this reduction in grain size originated from the formation of the secondary crystalline phases. The roughness varied from 5 to 9 nm in thin films deposited on silicon (0 0 1) substrate and from 9 to 11 nm in thin films deposited on fused silica.

3.3. Optical properties

Fig. 5 shows the optical transmission spectra of the BBO:4%TiO₂, BBO:8%TiO₂ and BBO:16%TiO₂ thin films crystallized at 650 °C/2 h.

The value of the transmittance used as reference is a direct measure using the He–Ne laser (λ = 632.8 nm) wavelength. Other optical properties, such as the band gap and the cut-off, were obtained indirectly. Considering the high absorption region, the transmittance T
followed a simple correlation with absorption coefficient [23,24]:

\[ T = A \exp(-\alpha d) \]  

(4)

where \( A \) is approximately equal to the unity at the absorption edge and \( d \) is the thickness of the thin films. The relation between the absorption coefficient \( \alpha \) and incident photon energy \( h\nu \) for allowed direct and indirect transitions, respectively, can be written as [25]

\[ \alpha h\nu = A_1 (h\nu - E_g^1)^{1/2} \]  

(5)

\[ \alpha h\nu = A_2 (h\nu - E_g^2)^2 \]  

(6)

where \( A_1 \) and \( A_2 \) are two constants and \( E_g^1 \) and \( E_g^2 \) are the direct and indirect band gaps, respectively.

The \((\alpha h\nu)^2\) vs. \( h\nu \) plots for thin films containing different amounts of TiO\(_2\) are shown in Fig. 6. A linear behavior can be observed in a certain range of the curves, supporting the interpretation of direct \( E_g^1 \) band gap for thin films [23]. Therefore, the \( E_g^1 \) band gap of the thin films can be obtained by extrapolating relation Eq. (5) between 3.85 and 5.57 eV. Table 2 gives a comparison of the \( E_g^1 \) band gap with the TiO\(_2\) content. As can be seen, the band gap of thin films decreases from 5.57 for 3.85 eV as the TiO\(_2\) concentration increases from 4 to 16 mol\%. The increase of the TiO\(_2\) concentration to 16 mol\% reduces the band gap, thus increasing the conductive nature of thin films. Formation of the BaTiO\(_3\) phase as the TiO\(_2\) concentration increased from 4 to 16 mol\% was probably the main reason for the differences found in the optical properties. According to the literature, the cut-off in BaTiO\(_3\) thin films with different crystallite sizes and deposited on fused silica by the r.f. magnetron sputtering technique varies between 330 and 350 nm, while the band gap varies from 3.53 to 3.68 eV [26]. Terashima et al. [27] observed a similar effect in their study of glasses of the BaO–B\(_2\)O\(_3–\)TiO\(_2\) system. The optical properties of thin films with a BBO:4\%TiO\(_2\) composition obtained by the modified polymeric precursor method are very similar to those of \( \beta\)-BBO single crystals: the \( \beta\)-BBO phase in single crystal form possesses a cut-off at 190 nm, transmittance of approximately 80\% and a 6.2-eV band gap [28].

The thin films deposited on fused silica and synthesized at 650 °C were exposed to an incident beam of 1064 nm from a Nd:YAG laser. Fig. 7 shows the light transmitted from the \( \beta\)-BBO thin film of composition BBO:4\%TiO\(_2\) on fused silica and that of the fused silica itself, referred to as background. The intense emission at 532 nm indicates that our thin film displayed the

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**Table 1**

 Grain size and roughness of thin films containing 4, 8 and 16 mol\% of TiO\(_2\) on fused silica and silicon (0 0 1) substrates

<table>
<thead>
<tr>
<th>TiO(_2) (in mol%)</th>
<th>Grain size (nm)</th>
<th>Roughness (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Fused silica</td>
<td>Silicon (0 0 1)</td>
</tr>
<tr>
<td>4</td>
<td>135 ± 6</td>
<td>100 ± 7</td>
</tr>
<tr>
<td>8</td>
<td>93 ± 5</td>
<td>92 ± 5</td>
</tr>
<tr>
<td>16</td>
<td>82 ± 5</td>
<td>83 ± 5</td>
</tr>
</tbody>
</table>
Fig. 5. Optical transmission spectra of the thin films deposited on fused silica substrate: (a) 4 mol%, (b) 8 mol% and (c) 16 mol% of TiO₂.

Fig. 6. Absorption coefficient as a function of incident photon energy in the near band gap region for thin films deposited on fused silica substrate: (a) 4 mol%, (b) 8 mol% and (c) 16 mol% of TiO₂.

Table 2
Band gap, cut-off and transmittance and comparison with TiO₂ content of the thin films on fused silica substrate

<table>
<thead>
<tr>
<th>TiO₂ (in mol%)</th>
<th>Band gap (eV)</th>
<th>Cut-off (nm)</th>
<th>Transmittance at 632.8 nm (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>4</td>
<td>5.57</td>
<td>244</td>
<td>87</td>
</tr>
<tr>
<td>8</td>
<td>5.52</td>
<td>251</td>
<td>87</td>
</tr>
<tr>
<td>16</td>
<td>3.85</td>
<td>368</td>
<td>80</td>
</tr>
</tbody>
</table>

phenomenon of the SHG. An analysis of the efficiency of the SHG is currently in progress.

4. Conclusions

Using the modified polymeric precursor method, we prepared β-BBO thin films at temperatures as low as 650 °C with a high degree of preferential orientation in the (006) crystallographic direction in the thin films deposited on silicon (0 0 1) and fused quartz substrates and composition BBO:4%TiO₂. The degree of preferential orientation in relation to the (006) plane was comparable with that of thin films obtained by other deposition methods described in the literature.

Increasing the TiO₂ concentration induces a reduction in the grain size, which may occur in response to the formation of other secondary crystalline phases. The roughness of thin films deposited on silicon (0 0 1) varies from 5 to 9 nm and on fused silica it varies from 9 to 11 nm.

The optical properties of thin films with a BBO:4%TiO₂ composition obtained by the modified
polymeric precursor method are similar to those of β-BBO single crystals. An increase in the TiO₂ concentration induces the formation of the BaTiO₃ phase that causes reductions in the band gap, thus increasing the conductive nature of thin films.

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