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A New Calix[4]arene-Based Barium Precursor for $BaO-TiO_2$ Thin Film Deposition

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In the present work we describe the design, syntheses, and use of a new barium metalloorganic precursor for barium titanate thin film deposition. Barium-containing thin films deposited by different deposition methods are widely used for various applications in optics and electronics. An important goal for applications is concerned with the production of stable, fluorine free barium-metalloorganic precursor materials, to obtain better performance photonic devices. We describe an alternative barium-metalloorganic precursor based on a calixarene ligand, its application to dip coating and thin film growth of the $BaO-TiO_2$ family of compounds, and studies of these films by second harmonic generation. The $BaTiO_3$ films showed promising nonlinear optical response for guided wave-applications.

1. Introduction

Among the $BaO-TiO_2$ (BTO) family of compounds, the $BaTiO_3$ phase has received the most attention due to its promising electrooptical properties.[1] Nevertheless, more recent investigations have shown that other titanates such as $BaTi_4O_9$, $Ba_2Ti_9O_{20}$, and $BaTi_5O_{11}$ also exhibit attractive dielectric properties such as a low dielectric loss and a high dielectric constant which is temperature independent at microwave frequencies.[2] Among these titanates, $BaTi_5O_{11}$ is the least investigated.[3] In the present work we report on $BaTiO_3$ and $BaTi_5O_{11}$ thin film deposition by a dip coating (DC) technique. This method is suitable for large-area deposition and mass production and enables fabrication of thin films with high surface smoothness and optical quality. Interest in solution-derived methods for thin film processing such as spray coating, spin coating, and DC arises from the many potential advantages of those techniques. Many of these advantages have yet to be fully realized and reliably reproduced due, in part, to a large number of variables associated with the solution chemistry.[4] In particular sol−gel-based methods which make use of polymerization condensation reactions to form extended networks with chemical linkage suffer from irreproducibility due to poor viscosity and control over crystallization. The starting alkoxide precursors and their derivatives have to be nonmoisture-sensitive to avoid formation of gels instead of precipitate and have sufficient reactivity toward hydrolysis.[5] We were looking for a simple and technologically flexible method which is free of sol−gel-derived deficiencies. A mixed metal salt solution in a binder matrix,[6] which permits wide range viscosity control, seems to be a good candidate for obtaining perovskite films. However, barium oxide and barium salts have a limited solubility in the titanium butoxide when the binder is added. This led to the use of metaloorganic of barium that have higher solubility. The use of conventional barium β-diketonate or barium 2,2,6,6-tetramethyl-3,5-heptanedionate (THD) was shown to be limited due to the known poor storage stability of these precursors.[7] Stoichiometry control was difficult due to the formation of insoluble barium oxide and structure reproducibility was poor. A vital requirement for all deposition techniques is reproducibility in materials properties of the grown films. This motivated us to find an alternative stable barium precursor.

Thin film growth of barium-containing defect-free ferroelectric/photonic materials[8] and high-temperature superconductors[9] is highly dependent upon the metal-

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loorganic precursors, which often have low stability, such as for the "traditional" barium β-diketonate.[7] In other cases, control of the appropriate stoichiometric ratio of precursors can be problematic. Barium β-diketonate or barium 2,2,6,6-tetramethyl-3,5-heptanedionate (THD), which are regularly used as precursors, tends to decompose easily, generating components which are bound to the Ba^{2+} cation.[10] It is clear now that the barium diketonate derivative with the empirical formula $Ba(THD)_2$ can only be synthesized under rigorous anhydrous conditions[11] and that crystals of this composition contain tetrameric $Ba_4(THD)_8$ molecules.[12] The first synthesized barium complex $Ba_5(THD)_9(OH)\cdot 3H_2O$ is a mixed oligomeric species present in $Ba(THD)_2$ samples prepared by aqueous routes.[13] It is believed that the molecular size of these Ba_4 and Ba_5 complexes is too large for them to show the stability required in solution-derived deposition techniques. Consequently efforts have been focused on the preparation of the so-called adducts of $Ba(THD)_2$, ideally containing only one metal atom per two ligand molecules and stabilized by additional uncharged ligands attached to the metal center in order to saturate the coordination sphere of the metal. Polyethers, e.g., tetraglyme and hexaglyme,[14] ammonia,[15] pivalic acid,[16] and 2,5,8,11,14-pentaoxapentadecane,[17] have been added to barium β-diketonate in order to increase the lifetime of the barium THD precursors. Most of these studies dealt with the synthesis and structure of the compounds. These synthetic efforts resulted in fluorine-containing compounds of barium—[Ba(tdfnd)$_2$] (Htdfnd = 1,1,1,2,2,-3,3,7,7,8,8,9,9,9-tetradecafluorononane-4,6-dione) and its adduct with tetraglyme (2,5,8,11,14-pentanoxapentadecane).[18] The main disadvantage of using these precursors is film contamination with fluorine,[19] which in turn causes degradation in the electrical properties for high-temperature superconductors and the optical quality of ferroelectric/photonic materials. Aside from this, only polyether adducts of barium THD chelate have been used in chemical vapor deposition (CVD) growth of thallium-based superconductors[18] and barium titanate ($BaTiO_3$).[9a]

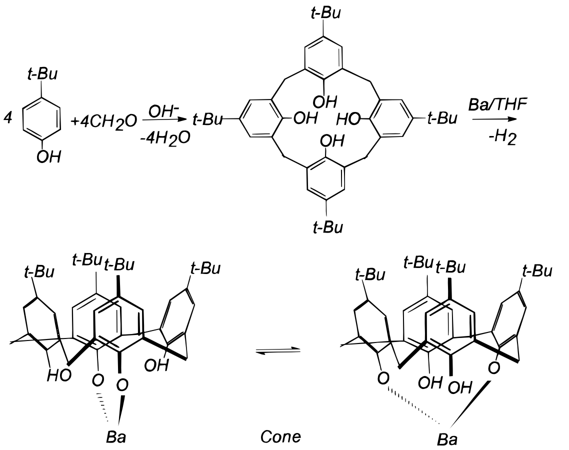

Figure 1. Synthesis of the barium calix[4]arene derivative.

We consider that despite attempts to attach stabilizing radicals to Ba−THD complex, the ionic size of barium is too large to form a stable metalloorganic compound with diketonate ligand.[7] Consequently we have tried a new *calixarene* ligand for a barium-containing metalloorganic complex.

As a precursor ligand we used the *tert*-butylated calix-[4]arene derivative: pentacyclo[19.3.1.1.1.1]octacosa-1(25),3,5,7(28),9,11,13(27),15,17,19, (26),21,23 -dodecaene-25,26,27,28-tetrol. The smallest *p-tert*-butylcalix[4]arene has a "cup-like" (in Greek: *calix*) form according to X-ray crystallography data.[20] We consider that incorporation of barium cation into the calixarene "cup" (see Figure 1) will result in the formation of a more stable metalloorganic precursor.

We report here the synthesis and structure of a new barium-containing metalloorganic compound based on a *calixarene* ligand.[20] This precursor is stable under prolonged storage and exposure to elevated temperatures. The barium-calixarene-derived complex, used as a precursor in solid single source OMCVD, exhibits excellent transport properties.[21a,b] This precursor compound was used for thin film growth of materials of the $BaO-TiO_2$ family via DC. In addition to $BaTiO_3$ thin film, we obtained, for the first time, $BaTi_5O_{11}$ thin films on sapphire.

2. Experimental Section

2.1. Synthesis of Barium-Containing *p-tert*-Butylcalix-[4]arene. Here we use an abbreviation, Ba(C[4]A), to desig-

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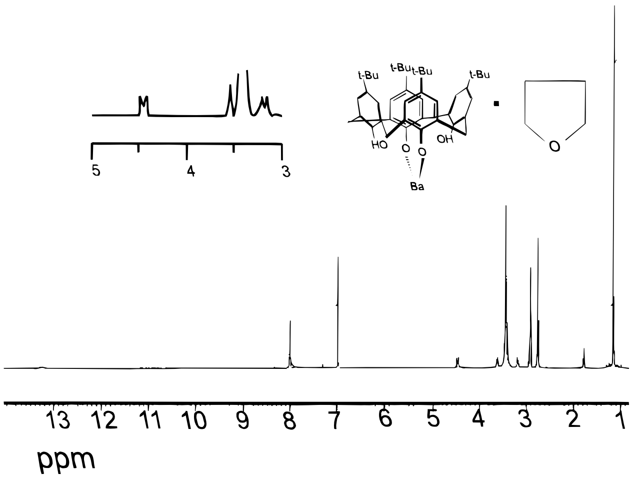

Figure 2. ^{1}H NMR (400 MHz, DMF-d_7, rt) spectrum of the Ba(C[4]A). Inset: structure of doublets at 3.12 and 4.42 ppm.

nate the barium salt of the *p-tert*-butylcalix[4]arene. The calixarene ligand was synthesized according to a published procedure.[20] Two different forms of this complex were obtained. The first, form A (Figure 1), was synthesized by placing metallic barium powder (1.05 g, 8.39 mmol) into 250 mL of dry THF (dried by distillation from Na/K alloy), followed by dropwise addition of *p-tert*-butylcalix[4]arene (5.00 g, 7.71 mmol) dissolved in 150 mL of dry THF, while stirring over the period of 1 h at 60 °C. The mixture was then refluxed under an Ar atmosphere for another 90 h. The product was filtered, washed with THF (3 × 300 mL), and dried under reduced pressure (yield 76%, 4.59 g). ^{1}H NMR (400 MHz, DMF-d$_7$, rt) δ: 1.15 (s, 36H, *t*-Bu); 3.12−4.42 (d, 8H, (CH$_2$)); 6.9 (s, 8H, aromatic rings); 13.25 (broad singlet, 2H (OH)); 1.75, 1.36, signals present only in form A spectrum; 3.45, H$_2$O was absorbed by hygroscopic DMF-d$_7$ solvent; 2.75; 2.9; 8.05, DMF.

It was verified by ^{1}H NMR that form A contains also one adduct molecule (1:1 molar ratio) of THF (Figure 2). The second, form B, was obtained by dissolving form A in ethanol and then removing of undissolved materials by centrifugation followed by solvent evaporation under reduced pressure. The absence of the adduct THF molecule in form B was demonstrated by the absence of THF peaks in the ^{1}H NMR spectra of form B, while all other peaks of form A were retained.

Preparation of both forms does not require rigorously dry conditions, such as in the Schlenk line technique and/or the use of a glovebox. These methods are usually applied in the synthesis of new barium-containing metalloorganic materials.[12] Both products have high hydrolytic and thermal stability, do not require special storage conditions, and are available for use as powdered solid and in solution form.

2.2. Spectroscopic Investigation of Ba(C[4]A) Precursor. NMR spectra were recorded on a AMX-400 MHz pulsed FT spectrometer using *N*-dimethylformamide-d_7 (DMF) as solvent. Raman spectra were recorded using a Spectra-Physics Model 164 Ar$^+$ laser, a SPEX Model 1401 double monochromator, and a cooled GaAs photomultiplier. The 488 nm laser line with a line width of 150 and 200 mW was used for excitation with spectral resolution of 5 cm^{-1} and scanning speed of 100 cm^{-1}/min. The powder samples under examination were placed in sealed capillaries. IR spectra were recorded using the Bruker FT-IR spectrometer, Model IFS 113v, with spectral resolution of 2 cm^{-1}. Samples with 1% concentration Ba(C[4]A) precursor in KBr pressed powder pellets were used.

2.3. BaO−TiO$_2$ Family Thin Film Deposition Using Ba(C[4]A) Precursor. BaTiO$_3$ and BaTi$_5$O$_{11}$ thin films were obtained by dip coating (DC) on a sapphire substrate followed by heat treatment in a vacuum oven at $T = 100$ °C and reduced pressure of 1.8 × 10^{-2} Torr for 10 h and then in an O$_2$ flow oven at $T = 800$ °C for 12 h. The starting materials were Ba(C[4]A) precursor "form B", mixed with titanium butoxide in stoichiometric ratio for obtaining BaTiO$_3$ and BaTi$_5$O$_{11}$ phases, respectively. Poly(4-vinylpyridine) (MW = 50 000; Mercury Co.) and poly(ethylene glycol) (MW = 35 000; Aldrich Co.) were added in a mass ratio of 4:1 to the resulting solution in order to increase viscosity. The speed of the dip coating was in the range 0.4−0.8 mm/min. The resulting films had a transparent mirror-like surface.

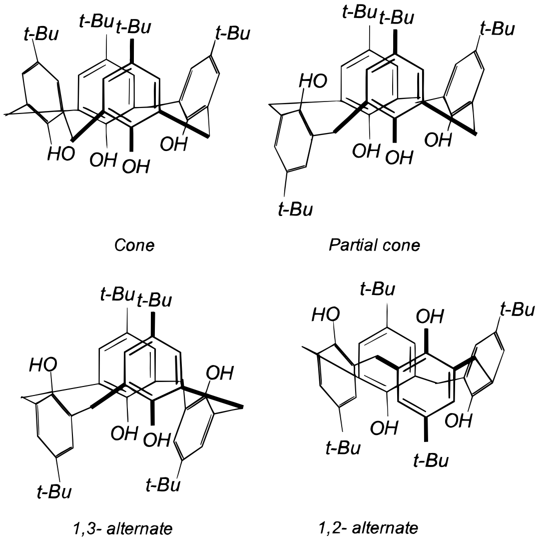

Figure 3. Conformations of the *p-tert*-butylcalix[4]arene.

2.4. SHG and Spectroscopic Ellipsometry Studies. The nonlinear optical response of the BaTiO$_3$ thin film was evaluated by second harmonic generation (SHG). The experimental setup for thin film nonlinear optical (NLO) measurement consists of a commercial Nd:YAG, Q-switched laser ("Surelite" Continuum Co.), emitting 7 ns pulses at 1.064 μm. A p-polarized beam with a spot diameter of 7 mm is directed into the sample. The sample is mounted on a computer-controlled rotation stage with the axis of rotation perpendicular to the propagation plane. The SH signal passes through an analyzer and is filtered with a narrow band 3 nm FWHM interference filter (at 532 nm). The signal is detected by a photomultiplier (Hamamatsu R955) connected to a fast scope. Spectroscopic ellipsometer WVASE32 (J. A. Woollam Co.) covering the 300−1700 nm spectral range was used for film thickness evaluation.

3. Results and Discussions

3.1. Structure Interpretation of Ba−Calixarene Complex. Although the Ba(C[4]A) complex was not obtained in the form of a single crystal, useful structural information has been extracted from the analysis of its ^{1}H NMR spectrum (Figure 2). The special property of the calixarenes lies in their three-dimensional structure. Analysis of space-filling molecular models show that calixarenes can never be planar. The calixarenes may in principle exist in a large number of conformations. The conformational preferences of a calix[4]arene are usually discussed in terms of four ideal conformations: "cone", "partial cone", "1,2-alternate", and "1,3-alternate" (Figure 3). These conformations are interconvertible by rotation of the phenolic moieties about the aromatic-methylene bridge.[20] The two sharp doublets of methylene protons in the ^{1}H NMR spectra at 3.12 and 4.42 ppm (Figure 2) indicate that there is a fixed "cone" conformation of the barium derivative of the *p-tert*-butylcalix[4]arene, as shown in Figure 3.[20] We have observed in Ba(C[4]A) only half (i.e., two) of the complex OH groups which are present in nonsubstituted *p-tert*-butylcalix[4]arene (Figure 3). This fact points out that there is one Ba^{2+} cation in Ba(C[4]A), which is ionically bonded to *p*-*tert*-butylcalix[4]arene^{2-} anion. These bonds have ionic character and thus determinate, in turn, the ligand exchange character of the (calixarene)$^{2-}$ with Ba^{2+}. These bonds change their connection to the different phenol groups, and these transformations are too fast relative to the NMR timescale (time of NMR pulse scanning). The equivalence of all *tert*-butyl groups and all aromatic protons of the Ba(C[4]A) molecule indicates a fast exchange process as shown in Figure 1.

3.2. Comparison of IR and Raman Spectra of Ba(C[4]A) Precursor with Calixarene Ligand. The important features of the IR and Raman spectra of the Ba(C[4]A) precursor and calixarene free ligand are summarized as follows: (a) The main difference between the Raman spectra of Ba(C[4]A) and the pure ligand consists of a shift of an intense singlet of the ligand at 73 cm^{-1} to an intense doublet at 85 and 92 cm^{-1} for Ba(C[4]A) accompanied with the appearance of strong singlet at 135 cm^{-1}. It was suggested[21] that the low-frequency region of the Raman spectrum provides a sensitive measure of metal−ligand vibrations for barium β-diketonates. On this basis we suggest that the observed shift and appearance of new bands is due to formation of the Ba(C[4]A) complex and is attributed to the metal−ligand vibration. (b) Three medium intensity lines at 667.5, 712.5, and 799.0 cm^{-1} appear in the IR spectrum of the Ba(C[4]A), while three lines of medium intensity at 782.0, 1199.1, and 1739.2 cm^{-1} in the starting ligand are absent. (c) We interpret the Ba(C[4]A) IR spectra as follows: 469.3 cm^{-1} is assigned as γ(C−O) out of plane deformation and 1699 cm^{-1} as C−O stretch in enol form. The vibrational structure of Ba(C[4]A) in the 900−1300 cm^{-1} range (called the "chelate-carbonyl region") coincides with the ligand spectra, except for one ligand band at 782.0 cm^{-1}.

The main spectral differences, related to formation of the Ba(C[4]A) compound, are situated in the low-frequency region of the Raman spectrum. These changes are indicative of metal complexation accompanied by metal−ligand bond formation. The observed changes in IR spectra are attributed to the changes in vibration of a phenolic hydroxyl that is transformed to an enolate−barium bond; similar characteristics in this spectral region (600−800 cm^{-1}) are observed for the related barium β-dekitonates.[21c] On the basis of IR and Raman spectral comparison of Ba(C[4]A) and the starting calixarene ligand, we confirm the formation of a new metalloorganic compound.

3.3. Stability of Ba−Calixarene Precursor. It is noteworthy that both forms of Ba(C[4]A) "A and B" were stable after 12 months storage (under regular laboratory conditions) without any signs of "aging" or decomposition, as was evident by ^{1}H NMR, Raman, and FT-IR spectroscopic examinations. This exceptional stability differs from the conventional Ba β-deketonate precursor that exhibits poor aging stability.[21] Moreover, the high thermal stability of the new precursor is evident by the preservation of the ^{1}H NMR spectrum of the Ba(C[4]A) following exposure to 100 °C for 5 h.

3.4. Thin Films Characterization. (*a*) *$BaTi_5O_{11}$ Films on Sapphire.* The $BaTi_5O_{11}$ phase was predicted by Roth[23] on the basis of O'Bryan's data,[24] and the crystal was reported later by Tillmanns.[25] It was suggested that this phase could exhibit superior dielectric properties under single-phase conditions. However further investigation of the $BaTi_5O_{11}$ phase[26] revealed many defects in its lattice images, and poor reproducibility in single-phase growth was attributed to structural inhomogenieties. It is also recognized that the synthesis conditions in these thin film BaO−TiO_2 systems were far from being controlled.[8] Here we report a very simple and straightforward route toward the fabrication of $BaTi_5O_{11}$ thin films: the XRD spectrum of the $BaTi_5O_{11}$ thin films (Figure 4) exhibit (200/220) texture with very sharp and narrow intense lines. This structural regularity of the deposited thin films opens up a new possibility of studying this important member of the BTO family. The $BaTi_5O_{11}$ thin films were found to be SHG inactive. The ellipsometry derived thickness of a $BaTi_5O_{11}$ thin film prepared via this route was 185 nm.

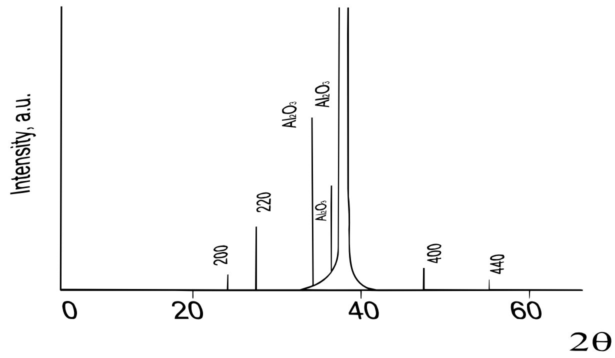

Figure 4. XRD of $BaTi_5O_{11}$ thin film on sapphire, (110) textured.

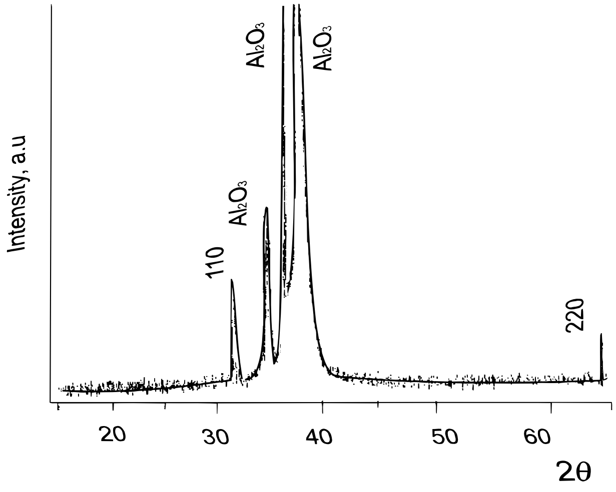

Figure 5. XRD of $BaTiO_3$ thin film on sapphire, (200/220) textured.

(*b*) *$BaTiO_3$ on Sapphire.* $BaTiO_3$ films were characterized with a high percent of (220) texture component, with a minor amount of host phase, which can be identified as a $BaCO_4$ phase, as can be seen in X-ray powder diffraction (XRD) using Cu Kα radiation (Figure 5). The ellipsometry-derived thickness of a $BaTiO_3$ thin

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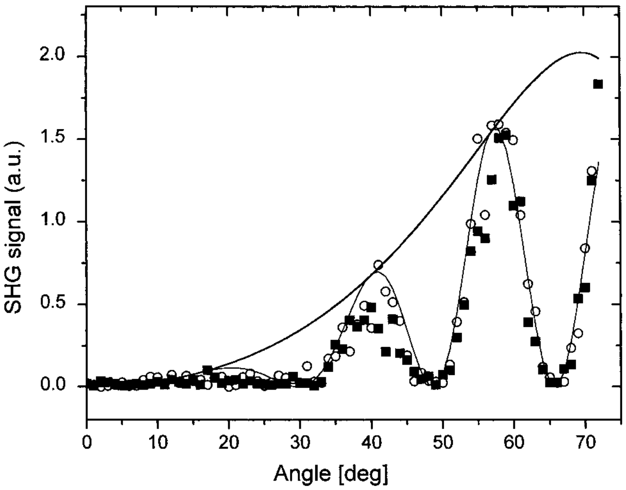

Figure 6. Experimental and theoretical fit for the SH signal as a function of incidence angle. The samples are in the Y configuration: bare sapphire (filled squares); sapphire + $BaTiO_3$ layer (open circles); theoretical fit (full line) of envelope and the fringe pattern.

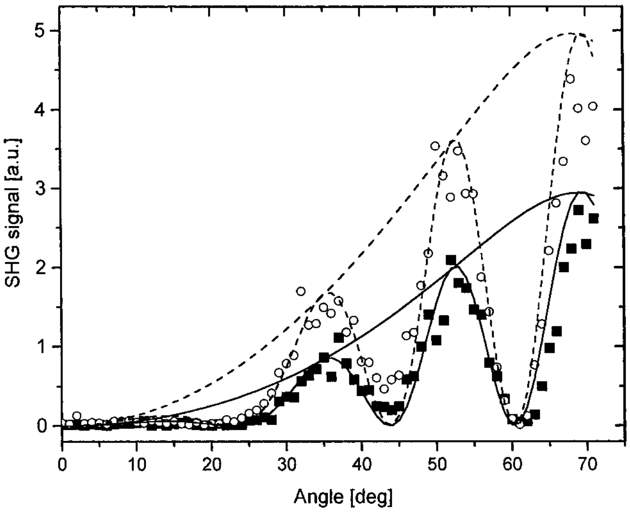

Figure 7. Experimental and theoretical fit for the SH signal as a function of incidence angle for a X configuration measurement. Fitting curves are given separately for the bare sapphire sample (full line) and the sapphire + $BaTiO_3$ sample (dashed line). Due to the birefringence of sapphire, the interference maxima are observed at different angles than those in Figure 6.

film on sapphire was found to be 259 nm. It is interesting to note that the (220) texture obtained in this work was different from the texture of $BaTiO_3$ deposited by OMCVD on a $LaAlO_3$ substrate (200) [see ref 8a] that was already (200) textured.

We have measured SHG from a 0.5 mm thick plate of sapphire covered on both sides with a $BaTiO_3$ thin layer 0.25 mm. Measurements were performed for two orthogonal crystal orientations and by rotating the crystal around the axis normal to the plane of incoming p-polarized laser beam and detecting p-polarized SHG. In the first measurement the crystal y-axis is parallel to the rotation axis (Y configuration) while in the second case the x-axis is parallel to the rotation axis (X configuration). Starting with a bare sapphire sample, we observed a slightly stronger SH signal in the X configuration. Since sapphire is a centrosymmetric crystal, its SH signals are generated at the surface only and are due to the $\chi^{(2)}{}_{zzz}$, $\chi^{(2)}{}_{yzy} = \chi^{(2)}{}_{zyy}$, and $\chi^{(2)}{}_{xzx} = \chi^{(2)}{}_{zxx}$ coefficients. For the $BaTiO_3$ film sample on sapphire, the SH signal obtained for the Y configuration has the same magnitude as that obtained with sapphire in the same direction (Figure 6). Therefore we conclude that there is no contribution to the SH signal from the $BaTiO_3$ layer in this geometry. The fringe pattern is a result of interference of SH waves originated at two surfaces. The expression of fringe maxima is consist with the dispersion ($n_{532}-n_{1064}$) for 0.5 mm thick Al_2O_3. For X configuration the $BaTiO_3$ contribution to the signal is considerable (Figure 7). Since the signal in the Y configuration for sapphire and for $BaTiO_3$ on sapphire are similar, it is assumed that nonlinear polarizability tensor elements $\chi^{(2)}{}_{zzz}$ and $\chi^{(2)}{}_{xzx}$ of $BaTiO_3$ are negligible and only the $\chi^{(2)}{}_{yzy}$ coefficient of the $BaTiO_3$ contributes to the observed increase in SH signal. Figures 6 and 7 show theoretical fits to the envelopes of the measured SH signals. The fits are obtained by keeping the $\chi^{(2)}{}_{zzz}$ coefficient as a constant and varying the ratio of $\chi^{(2)}{}_{yzy}$ and $\chi^{(2)}{}_{xzx}$ to $\chi^{(2)}{}_{zzz}$ in order to get a satisfactory fit to the measured angular dependence of the SH signal. We obtained the following results: (a) for bare sapphire sample, $|\chi^{(2)}{}_{yzy}/\chi^{(2)}{}_{zzz}| = 0.26$; (b) for a sapphire + $BaTiO_3$ sample, $|\chi^{(2)}{}_{yzy}/\chi^{(2)}{}_{zzz}| = 0.39$. The ratio $|\chi^{(2)}{}_{xzx}/\chi^{(2)}{}_{zzz}|$ is the same for both samples with a value of 0.18.

Sapphire is considered to be a less suitable substrate for the deposition of optical quality films,[27] and the most popular substrates for BTO thin film depositions are MgO[25] and $LaAlO_3$.[29] We show in this work that it is possible to obtain films with high optical quality on sapphire. This, in turn, opens the way for the fabrication of NLO active waveguide devices by processing the waveguide on a sapphire substrate which has very attractive microwave properties such as low microwave loss tangent $\delta \approx 10^{-8}$ and low relative dielectric permittivity $\epsilon \approx 5-12$.[30]

4. Conclusions

In this contribution we reported the synthesis of a new barium metalloorganic compound based on calixarene as an alternative barium-containing precursor for thin film deposition. Structural analysis of this precursor was verified by NMR, IR, and Raman spectroscopies. This new precursor is very stable over long storage times and on exposure to elevated temperatures. Thin films of the BTO family were obtained by DC, using the novel barium precursor, the barium-calixerene derivative. The properties of the resulting BTO films were studied by XRD, and $BaTiO_3$ was also studied by SHG measurements. The SH generated in the thin $BaTiO_3$ film is attributed to the $\chi^{(2)}{}_{yzy}$ tensor component of $BaTiO_3$ which is nearly twice that obtained from the sapphire surface. The dominant off-diagonal $\chi^{(2)}$ term for the $BaTiO_3$ on sapphire is similar to the one that has been observed for single-crystal $BaTiO_3$.[31]

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We propose that Ba-calixarene can be used as a precursor for Ba-containing thin films by various deposition techniques both in solid and liquid form. We hope that the new organometallic material will provide an alternative method to overcome the known instability of the barium-containing precursors for thin film deposition.

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Supporting Information Available: Table of IR and Raman spectral data of the Ba(C[4]A) precursor and the free calixarene ligand (1 page). Ordering information is given on any current masthead page.

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