Revealing the Role of the Intermediates during the Synthesis of BaTi$_5$O$_{11}$

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**ABSTRACT**

BaTi$_5$O$_{11}$ has been extensively studied because of their microwave dielectrics properties. Traditionally, it is difficult to achieve this material as single-phase. Here, we report an effective method to obtain BaTi$_5$O$_{11}$ powder with nanometer-scale crystals, by solid-state reaction at moderate temperatures and using as precursors nanostructured particles consisting of BaTiO$_3$ and TiO$_2$. The main advantage is the intimate contact between the BaTiO$_3$ and TiO$_2$ that ensure, when the solid-state reaction takes place, the formation of complex solid compounds from three or more constituents. The formation mechanism of BaTi$_5$O$_{11}$ has been studied as a function of both the thermal treatment and the time reaction. The reaction was monitored by Raman spectroscopy combined with Confocal microscopy, the aim of this characterization technique is to provide the description of the general strategy and design principles to obtain BaTi$_5$O$_{11}$ powder. Consequently, this work is a challenging task for the compositional and structural study of complex inorganic nanoparticles.
INTRODUCTION

The different crystalline phases present in the binary system of BaTiO$_3$-TiO$_2$ exhibit excellent microwave properties.$^1$ Specifically, BaTi$_5$O$_{11}$ ceramic has demonstrated potent functional dielectric characteristics, resulting in an interesting advanced material for microwave communications.$^2$–$^4$ Owing to its high interest, BaTi$_5$O$_{11}$ powder as a single-phase has been the subject of research, and a great number of researchers have tried to produce this material in a variety of ways. O'Brien and Thomson$^5$ synthetized BaTi$_5$O$_{11}$ by the traditional ceramic method, such as the solid-state reaction of BaCO$_3$ and TiO$_2$ at high temperatures (1100 - 1400 $^\circ$C), however, this method could not produce single-phase material. Ritter et al.$^6$ produced the BaTi$_5$O$_{11}$ compound by a controlled hydrolysis. They relied on O'Brien's study, to predict the excellent dielectric properties of the BaTi$_5$O$_{11}$ material. Other chemical processes were effectively used to obtain the fine powder of BaTi$_5$O$_{11}$ as single-phase. Fukui et al.$^7$ reported the effects of the thermal treatment on the sintering of BaTi$_5$O$_{11}$ ceramics from an alkoxide-derived powder. Employing a liquid-mix method, Javadpour and Eror$^8$ obtained BaTi$_5$O$_{11}$ by calcining the mixture obtained after the reaction of tetraisopropyl titanate, barium carbonate and an ethylene glycolcitric acid solution. Lu et al.$^9$ and Tangjuank et al.$^{10}$ obtained BaTi$_5$O$_{11}$ powder using a sol-gel process, in both cases the precursors were sintered at temperatures from 700 to 1200 $^\circ$C. In addition, the evolution in the structure of intermediates, the mechanism involved during the reaction, and the final morphology of BaTi$_5$O$_{11}$ material, because of the thermal processing, are still not clearly defined.$^{10}$
Chemical reactions may be optimized by reaction monitoring because it provides information about the chemical development at every stage of the reaction system. Transmission Electron Microscopy (TEM) and X-Ray Diffraction (XRD) are currently used to structurally determine the reaction phases. However, reaction in nanostructured materials still represents a challenge because the structural analysis of nanoregions is limited in multiple phases systems. Confocal Raman microscopy is a powerful tool for research, which may introduce significant enhancements over other common analytical techniques. It is a non-destructive, non-invasive, and contact- and label-free technique and discloses evidences about the stress and strain states, crystal structure, electronic properties and lattice vibrations. Consequently, it permits detecting the different phases present in the materials. Moreover, the combination of confocal Raman spectroscopy and Confocal microscopy, allows us to systematically study the structure–microstructure of a wide variety of materials and composites, as well as to resolve the spatial distribution of the compounds, owing to the high spectral and spatial resolution of this technique. In this sense, Raman spectroscopy is an effective technique for the characterization of the different phases obtained during a solid-state reaction.

In conclusion, this work will contribute to study the thermal evolution of core-shell BaTiO₃/TiO₂ nanoparticles to obtain single-phase BaTi₅O₁₁ particles. BaTiO₃ nanoparticles were synthesized through a hydrothermal method and consequently coated accordingly with a TiO₂ shell. Therefore, the samples were characterized by Raman Spectroscopy, X-Ray Photoelectron Spectroscopy (XPS) and X-Ray Diffraction (XRD); in order to evaluate the behaviour of the
reagents used for the preparation of the core-shell particles and its effects in the solid-state reaction during the thermal treatments.

**EXPERIMENTAL PROCEDURE**

**Synthesis:**

The synthesis of barium titanate particles was accomplished following this chemical reaction:\(^1\)

\[
\text{BaCl}_2 \text{(aq)} + \text{TiOCl}_2 \text{(aq)} + 4\text{NaOH (aq)} \rightarrow \text{BaTiO}_3 \text{(s)} + 4\text{NaCl (aq)} + 2\text{H}_2\text{O (l)}
\]

where (aq) designates an aqueous solution.

The reaction was performed in a continuous Segmented Flow Tubular Reactor (SFTR), similar to that used by Jongen et al.\(^1\) The reaction was carried out at 95\(^\circ\)C and the residence time in the tubular reactor (length, 12 m, inner diameter, 4 mm) was 10 min. The BaTiO\(_3\) precipitate obtained after reaction was centrifuged, it should be washed with water until it was free from chloride ions, and finally dried. Additional details about the preparation and properties of the barium titanate particles used as templates can be found at the Supporting Information.\(^1\,2\)

The previous obtained BaTiO\(_3\) particles were introduced in a peroxotitanium (IV) solution (prepared as described in the Supporting Information), under continuous slow stirring at room temperature. The amount of Ti (IV) solution spent for the coating process was calculated to have an overall stoichiometry corresponding to Ti/Ba = 5. The suspension was maintained at 95\(^\circ\)C for 1 h. The resulting yellow powder, was then filtrated, washed with water until it was free from chloride ions, and finally dried.

Finally, the resulting BaTiO\(_3\)/TiO\(_2\) powders were introduced in a cylindrical steel body of 1 cm in diameter, and they were compacted by isostatic cold pressing.
Then, sintering was carried out, in a conventional muffle furnace, at different temperatures between 400°C to 1000°C with a heating rate of 5ºC/min. The hold time at the maximum temperature was 1 minute in each treatment.

**Characterization:**

The crystalline structure of the samples was studied by X Ray Diffraction (XRD) in a D8 Bruker Diffractometer with Cu Kα radiation and a Lynx Eye detector. Differential thermal (DTA) analysis joined to thermogravimetric (TG) analysis was carried out to study the thermal behaviour of the materials by using a Netzch STA 409 Thermo-Analyzer. The assay conditions correspond to the synthesis process: 20-1400 ºC with heating rate of 5 ºC/min.

A XPS study determined the surface composition of the samples in a K-Alpha, Thermo Scientific equipment applying pass energy of 200 eV for survey scans and 40 eV for high resolution scans, and shifting the C 1s peak to 285 eV.

The morphology of the particles was observed by using a Field Emission Scanning Electronic Microscope, FESEM, S-4700 from Hitachi. The morphological parameters were obtained by processing FESEM micrographs with Leica Qwin Image software. The obtained results consisted of a statistical study of values from more than 150 measured particles.

A confocal micro-Raman Witec α 300R equipment equipped with 532 nm excitation laser was using to achieve a Raman study of the samples by applying an incident laser power of 40 mW. The results treatment was carried out with a Witec Control Plus Software.

**RESULTS AND DISCUSSION**

The crystalline structure of the precursors is determined by XRD (*Figure 1*). *Figure 1a* shows that the as-precipitated BaTiO₃ particles possess the typical
pseudo-cubic structure of hydrothermal particles (JCPDS 01-075-0214). In addition, it is possible to distinguish the presence of BaCO\textsubscript{3} (JCPDS 00-001-0506), despite the precautions taken during the synthesis. Figure 1b-c show the XRD patterns of the BaTiO\textsubscript{3}/TiO\textsubscript{2} particles, both as prepared and after 10 days aging. The diffractogram of the freshly prepared sample are characterized by the superposition of narrow diffraction peaks corresponding to the cubic BaTiO\textsubscript{3} and a broad hump at 25-35\degree 2\theta that could be associated with the amorphous titania phase.\textsuperscript{21,22} After 10 days of aging, the diffraction peaks of BaTiO\textsubscript{3} almost disappear leaving only the characteristic diffraction spectrum of amorphous hydrated titania, which does not reveal any crystal characteristics; it only shows two wide bands, one centred at \(~32\degree\) 2\theta and the other at \(~50\degree\) 2\theta.\textsuperscript{23} According to the previous studies,\textsuperscript{24-27} the amorphous phase of peroxo-titanium hydrate with a unknown structure is generated when the spontaneous hydrolysis at room temperature of the peroxo-titanium solution occurs.\textsuperscript{23} In the temperature range of 80-100 \degree C, the peroxo-titanium hydrate evolves towards the formation of an amorphous hydrated titania.\textsuperscript{25-27} Consequently, we suggest that the amorphous layer achieved in this work consists mainly of an amorphous titania comprising hydration water.\textsuperscript{23,28}

The Raman spectrum for as precipitated BaTiO\textsubscript{3} sample shows the typical spectrum for BaTiO\textsubscript{3} in a psedocubic phase (Figure 1d). This polymorph is based on cubic \textit{Pm\textsubscript{3}m} (Oh\textsubscript{1}) symmetry and the phonon modes are represented by 3F\textsubscript{1u} + F\textsubscript{2u}.\textsuperscript{29} Although no Raman-active mode is predicted for the cubic phase, it has been reported that it typically shows two wide Raman bands at around 250 and 520 cm\textsuperscript{-1}.\textsuperscript{29-32} The as precipitated BaTiO\textsubscript{3} presents Raman bands centred at ca. 299 and 521 cm\textsuperscript{-1}, which indicates local disorder of titanium atoms in a nominally
pseudocubic phase. Raman bands at 667 and 1059 cm\(^{-1}\) are also detected in the samples and are assigned to the BaCO\(_3\) phase\(^{30,33,34}\) while the Raman band at 181 cm\(^{-1}\) is attributed to the BaCl\(_2\) phase\(^{35-37}\) (a complete assignment of the BaCl\(_2\) spectrum is given in the Supplementary info, Figure S1). The Raman band at 807 cm\(^{-1}\) should have been caused by the deformation of hydroxyl lattice groups, they are located in the BaTiO\(_3\) structure as defects in oxygen sites.\(^{38,39}\)

The Raman spectrum of the 10 days aged precipitate of BaTiO\(_3\)/TiO\(_2\) sample shows several broad Raman features located at ca. 280, 380, 450, 670, 810 and 870 cm\(^{-1}\) (Figure 1e). These Raman bands correspond to the vibration modes of the Ti-O-Ti bonds.\(^{23,27,40}\) It is also worth highlighting that, the strong Raman band at 525 cm\(^{-1}\), which is characteristic of the Ti-O-O groups in gels composed of peroxy-titaniunm, is not observed in the 10 days aged precipitate.\(^{23,27}\) Thus, it could be excluded the existence of an important quantity of residual peroxy groups in the 10 days aged precipitated particles.

The morphology of as precipitates BaTiO\(_3\) nanoparticles is shown in the Figure 1f. The stoichiometric particles are small in size (\(\approx\)100 nm) and they have a nearly spherical shape.\(^{41}\) Moreover, into the Figure S2 it could be observed smaller primary particles (\(\approx\)100 nm), that are aggregated to build up the so obtained BaTiO\(_3\) particles.

According to similar previous studies,\(^{42}\) the amorphous titania coating generated onto the surface of barium titanate nanoparticles is owing to the hydrolysis of the peroxotitanium solution. The formation of the coating is promoted by the differences in surface potential between the BaTiO\(_3\) particles and the amorphous titania when the pH of the suspension was adjusted to 9. Thus, the amorphous titania self-assemble spontaneous at the barium titanate nanoparticle surface.\(^{23}\)
Furthermore, the morphology of the 10 days aged BaTiO$_3$/TiO$_2$ composite particles evidence the rearrangement of the primary particle of BaTiO$_3$ during the formation of the titania coating, *Figure 1g*. It may be noted that the size of the BaTiO$_3$/TiO$_2$ composite particles is slightly smaller than the BaTiO$_3$ nanoparticles (insets of *Figure 1f-g*), this fact confirms that the amorphous titania attacks the BaTiO$_3$ aggregates and therefore produces rearrangement. Moreover, the evolution of the crystallinity with the aging indicates that this attack also advance far from the disaggregation and promotes the reduction of crystallinity of the BaTiO$_3$ nanoparticles. This kind of chemical attack only could be justified if some reactant remains in the so obtained powder.

*Figure 1.*- Diffraction patterns of: (a) as obtained BaTiO$_3$ particles, (b) fresh BaTiO$_3$/TiO$_2$ composite particles and (c) 10 days aged BaTiO$_3$/TiO$_2$ composite particles. (The arrow indicates the peaks of amorphous titania). Raman spectrum
obtained for (d) as obtained BaTiO$_3$ particles, and (e) 10 days aged BaTiO$_3$/TiO$_2$ composite particles. (Peaks signalled as blue triangles (▼), green squares (■) and red stars (★) correspond to BaCO$_3$, BaCl$_2$ and internal defects, respectively).

FESEM micrographs of (f) as obtained BaTiO$_3$ particles and (g) 10 days aged BaTiO$_3$/TiO$_2$ composite particles. Particle size distribution of (h) as obtained BaTiO$_3$ particles and (i) 10 days aged BaTiO$_3$/TiO$_2$ composite particles.

A systematic surface characterization study of the particles was carried out by XPS, which is an effective technique to understand the chemistry produced at the surface of materials, because it provides evidences about the local bonding environment of the samples.$^{43,44}$ Moreover, it is a powerful tool for characterizing the chemical structure of nanoparticles at the surface and bulk.$^{45,46}$ A survey scan from 1300 to 0 eV (shown in Supplementary Info, Figure S3) indicated the existence of Barium, Titanium, Oxygen and Carbon in both the as obtained BaTiO$_3$ and 10 days aged BaTiO$_3$/TiO$_2$ particles. Additional high-resolution scans (Figure 2a-d) were conducted in the selected binding energy ranges for C$_{1s}$, O$_{1s}$, Ti$_{2p}$ and Ba$_{3d}$, respectively, in order to quantify the elemental composition of the samples. The C$_{1s}$ peak can be deconvoluted into two principal bands (see Figure 2a) with a peak centred at 285 eV, corresponding to the C-H/C-C species and the other one centred at 286.4 eV, due to C=O groups. The amount of the carbon atoms bonded as C-C/C-H and as C=O is 75% and 15%, respectively. These signals of carbon, owing to the environmental contamination, are assigned as absorbed carbon and absorbed CO$_2$. However, the C$_{1s}$ peak displays a third component at 288.9 eV for the as prepared BaTiO$_3$ particles and at 289.2 eV for the 10 days aged BaTiO$_3$/TiO$_2$ particles having a ~10% contribution and it has been assigned to CO$_3^{2-}$ ions.$^{47,48}$ The O$_{1s}$ signal displays also three components,
as seen in Figure 2b. For the BaTiO$_3$ particles, there is an intense band near 529.2 eV assigned to oxygen atoms in the Ba-O-Ti structure.$^{49,50}$ In the case of the aged BaTiO$_3$/TiO$_2$ particles, this peak appears at 530.1 eV and it is attributed to the oxygen atoms in Ti-O-Ti structure.$^{49,50}$ The peak at 530.5 eV (BaTiO$_3$ particles) or at 531.3 eV (aged BaTiO$_3$/TiO$_2$ particles) corresponds to the hydroxyl group on the surface of nanoparticles.$^{47}$ The O$_{1s}$ emission line at 531.7 eV (BaTiO$_3$ particles) or at 531.9 eV (aged BaTiO$_3$/TiO$_2$ particles) is assigned to the absorbed oxygen as O-C of CO$_2$. The fitted Ti$_{2p}$ spectrum for the core BaTiO$_3$ nanoparticles, Figure 2c, shows the main peaks assigned to Ti$_{2p}^{1/2}$ and Ti$_{2p}^{3/2}$ centred at 463.8 eV and 458.0 eV respectively, which are in good agreement with the bonding energies of Ti$^{4+}$ in BaTiO$_3$.$^{48}$ Whereas, the peaks detected at 464.4 eV and 458.6 eV in the XPS spectrum of Ti$_{2p}$ for the aged BaTiO$_3$/TiO$_2$ particles is assigned to the Ti$^{4+}$ in TiO$_2$.$^{51}$ Finally, the Ba$_{3d}$ spectra in both samples BaTiO$_3$ and BaTiO$_3$/TiO$_2$ look slightly different, Figure 2d. In the case of the BaTiO$_3$ particles there are two signals due to the Ba$_{3d}$ specie (Ba$_{3d}^{3/2}$ and Ba$_{3d}^{5/2}$) that can be deconvoluted into 2 peaks at around 793.8 eV and 795.2 eV, which is consistent to barium in titanate and in carbonate species, respectively. Moreover, for the Ba$_{3d}^{5/2}$ the two peaks located ca. 778.5 eV and 779.9 eV, also correspond to barium in titanate and in carbonate species, respectively. However, in the case of the aged BaTiO$_3$/TiO$_2$ particles the Ba$_{3d}$ peak can be resolved into Ba$_{3d}^{3/2}$ at 795.7 eV and Ba$_{3d}^{5/2}$ at 780.3 eV that it is assigned to barium in BaTiO$_3$ without presence of BaCO$_3$. It is worth nothing that for the BaTiO$_3$ sample was not detected chlorine from the BaCl$_2$, in contrast with Raman results: the Cl$_{2p}$ for the BaCl$_2$ should present a peak with a binding energy of 202 eV$^{52}$ that it was not present in the samples. Furthermore, the BaTiO$_3$ precipitated was carefully
washed with water. Accordingly with silver nitride test method\textsuperscript{53} the supernatant is chloride ions free. These two ideas may suggest that the BaCl\textsubscript{2} could be found between the BaTiO\textsubscript{3} aggregates.

\begin{figure}
\centering
\includegraphics[width=\textwidth]{XPS_spectra.png}
\caption{XPS spectra of as prepared BaTiO\textsubscript{3} (pink line) and aged BaTiO\textsubscript{3}/TiO\textsubscript{2} (green line) composite particles: (a) C\textsubscript{1s}, (b) O\textsubscript{1s}, (c) Ti\textsubscript{2p} and (d) Ba\textsubscript{3d} elements.}
\end{figure}

Based on the XPS analysis, the weight percentages of Ti, Ba, O, and C were also calculated and listed in Table1. The relative atomic percentages indicates that the Ba:Ti proportion of BaTiO\textsubscript{3} particles is 1:1, whereas for the BaTiO\textsubscript{3}/TiO\textsubscript{2} composite particles the Ba:Ti ratio is 1:4, which corresponds with the BaTi\textsubscript{4}O\textsubscript{9} compound. These data evidence that the BaTiO\textsubscript{3}/TiO\textsubscript{2} composite sample
presents Ba\(^{2+}\) cations at the surface that could be related to two aspects: a) diffusion effect during the synthesis process, or b) uncomplete covering of nanoparticles by the amorphous titania shell.

*Table 1.* Element contents (%) of core BaTiO\(_3\) and aged BaTiO\(_3\)/TiO\(_2\) composite particles based on XPS analysis.

<table>
<thead>
<tr>
<th>Sample</th>
<th>At % Ti</th>
<th>At % Ba</th>
<th>At % O</th>
<th>At % C</th>
<th>Ba:Ti</th>
</tr>
</thead>
<tbody>
<tr>
<td>BaTiO(_3)</td>
<td>13,70</td>
<td>14,34</td>
<td>48,85</td>
<td>23,11</td>
<td>1:1</td>
</tr>
<tr>
<td>BaTiO(_3)/TiO(_2)-10 days</td>
<td>16,71</td>
<td>4,54</td>
<td>47,38</td>
<td>31,37</td>
<td>1:4</td>
</tr>
</tbody>
</table>

*Figure 3* shows the thermal evolution study of the different samples (DTA/TG). The TG curve of both samples shown a first weight loss in the 40-200 °C temperature range, related to the evaporation of absorbed water. These mass losses continue gradually in the range 200-600°C related to the chemisorbed OH groups in the nanoparticle crystal lattice.\(^{54}\) Besides, the BaTiO\(_3\) nanoparticles shows two distinct mass losses at higher temperatures signalled by two DTG peaks. The first DTG peak, centered at \(\sim 816 \text{ °C}\), is associated with the thermal decomposition of BaCO\(_3\) and CO\(_2\) elimination in agreement of the endothermic peak observed at this temperature.\(^{55}\) At higher temperature, the second DTG peak (\(\sim 911 \text{ °C}\)) could be associated to the Cl\(^{-}\) removal in spite that the melting point of BaCl\(_2\) occurs at higher temperature and it is an endothermic phenomena.\(^{12}\) In the case of aged BaTiO\(_3\)/TiO\(_2\) composite, the thermogravimetric curves show the loss of adsorption water at temperatures <200°C and a weak exothermic peak at \(\sim 750 \text{ °C}\) without relevant mass variation, that could correspond to the phases crystallization. In order to determine the structural nature of such thermally activated reactions a XRD and Raman characterization it is afforded.
Figure 3. - DTA/TG analysis at a 5°C/min heating rate for the samples: (a) BaTiO$_3$ and (b) BaTiO$_3$/TiO$_2$ composite particles.

A XRD study of the samples after a thermal treatment at 1000°C is shown in Figure 4a-b. After thermal treatment at 1000°C, the BaTiO$_3$ sample present a main tetragonal structure (JCPDS 01-081-2205) with a minor secondary phase corresponding to the barium orthotitanate species, Ba$_2$TiO$_4$ (JCPDS 00-038-1481). The removal of barium carbonate observed in the precursor is in the origin of the appearance of such secondary phase. The as-prepared coated powder (BaTiO$_3$/TiO$_2$ composite) was also calcined in air at 1000°C and the diffractogram is shown in Figure 4b. The diffraction pattern for the BaTiO$_3$/TiO$_2$ composite heat-treated at 1000°C shows mostly the peaks of BaTi$_5$O$_{11}$ phase, in spite of their low resolution (JCPDS 00-035-0805). No evidence of other titanate phases are detected within the XRD resolution limit (of the order of 1 wt %). Hence, it can be asserted that the amorphous titania reacts with BaTiO$_3$ nanoparticles and the system evolves towards the formation of nanocrystalline BaTi$_5$O$_{11}$.

The Raman spectrum of the 1000°C thermally treated BaTiO$_3$ sample is shown in Figure 4c. The Raman modes centred at ca. 186 and 521 cm$^{-1}$ correspond to the transversal component of the mode with the A$_1$ symmetry (A$_1$ (TO)).$^{38}$ Whereas, the peak at ca. 719 cm$^{-1}$ can be assigned to the longitudinal mode of
A$_1$ symmetry (A$_1$ (LO)).$^{39}$ The Raman mode at ca. 307 cm$^{-1}$ is related to the B$_1$ mode, indicating asymmetry within the TiO$_6$ octahedral.$^{56}$ Finally, the Raman characterization for the 1000$^\circ$C thermally treated BaTiO$_3$/TiO$_2$ sample indicates the formation of BaTi$_5$O$_{11}$ is complete (Figure 4d).$^{8,9,57}$ In addition, it is observed a material densification in which grain boundaries and sintering necks appears in a nanostructured material having grain size ranging from 40 to 200 nm (Figure 4e-f).

Figure 4.- XRD patterns of 1000$^\circ$C thermally treated (a) BaTiO$_3$ and (b) BaTiO$_3$/TiO$_2$. Raman spectrum of 1000$^\circ$C thermally treated (c) BaTiO$_3$, and (d) BaTiO$_3$/TiO$_2$. FESEM micrographs of 1000$^\circ$C thermally treated (e) BaTiO$_3$ and (f) BaTiO$_3$/TiO$_2$.

Despite obtaining the desired phase, the role of intermediate compounds and the evolution of phase composition with temperature is not adequately resolved by
the use of XRD. To clarify this point both precursors are isothermally treated at 400, 500, 600, 700, 800, 900 and 1000°C for 1 h and Confocal Raman microscopy (CRM) has been used to determine the nature of intermediate chemical species and the evolution with the thermal treatment of main crystalline phases.

The CRM study of BaTiO$_3$ precursor at different temperatures has been carried out by mapping the surface of samples pressed into disks, Figure 5. Raman images of the untreated BaTiO$_3$ and 1000°C thermally treated BaTiO$_3$ samples are depicted to show the distribution of the main phases, Figure 5b-e and Figure 5f-i, respectively. The Raman images of the untreated BaTiO$_3$ sample, presented in Figure 5b-e, show three distinguishable phases: BaTiO$_3$ as the main phase (signalled by red regions, Figure 5b); BaCO$_3$ as disperse in agglomerates with a particle size of ~2 μm (signalled by blue region, Figure 5c); and unreacted BaCl$_2$ is distributed in the whole area where BaTiO$_3$ is present (signalled by green, Figure 5d). This fact, together with the convergence between BaTiO$_3$ and BaCO$_3$ in Figure 5b and Figure 5c, indicates that the BaCO$_3$ could be at the surface of the agglomerates, while the existence of unreacted BaCl$_2$ protects the BaTiO$_3$ against the carbonation. Figure 5a shows the average Raman spectrum of the core BaTiO$_3$ samples treated at different temperatures. The BaCO$_3$ disappears at temperatures >700°C (see Figure 5a), as signalled by the lack of the Raman signal at 1059 cm$^{-1}$ (in concordance with DTA-Tg study). It is worth noting that the unreacted BaCl$_2$ coexists with BaTiO$_3$ for the whole range of temperatures.
Figure 5. - (a) Average Raman spectra for BaTiO₃ thermally treated at selected temperatures. The main Raman modes of the different phases are signalled by colour-coding: BaTiO₃ in red; BaCO₃ in blue; and BaCl₂ in green. Raman images of the different phases for (b-e) untreated BaTiO₃ sample and (f-i) 1000°C thermally treated BaTiO₃ sample.

The evolution of average Raman spectra obtained for BaTiO₃/TiO₂ composite sample treated at various temperatures is shown in Figure 6a. The Raman image of the aged and untreated BaTiO₃/TiO₂, Figure 6b, only shows a broad Raman
band associated with Ti-O-Ti bonds, signalled by a magenta box. We study the Raman spectra as a function of the temperature treatment, between 400-700ºC (For the sake of brevity, this spectra is shown in the supplementary info, Figure S4 and it shows Raman peaks at 116, 140, 228, 264, 271, 362, 424, 630, and 845 cm⁻¹). As it was reported before, these Raman peaks correlate with the orthorhombic structure of BaTi₄O₉.⁵⁷–⁵⁹ In the Raman image (Figure 6e); it can be observed that the amount of the amorphous titanium decreases as the BaTi₄O₉ crystallize, signalled as yellow. In addition, the increase of the thermal treatment temperature favours the appearance of BaTi₅O₁₁ (signalled in cyan regions, Figure 6f). Taking into account the results of the Raman spectra, the system seems to have almost entirely transformed into BaTi₅O₁₁. Since this phase is observed from 800ºC and correlated with the crystallization denotes by an exothermic peak at ~750ºC in the DTA analysis (Figure 3b). The existence of crystalline BaTi₅O₁₁ is also in agreement with the XRD pattern of the 1000ºC thermally treated sample (Figure 4b).
Figure 6.- (a) Study of the Raman spectra evolution as a function of thermal treatment for the BaTiO$_3$/TiO$_2$ composite sample. The main Raman modes of the different phases are signalled by colour-coding: amorphous Ti in magenta; BaTi$_4$O$_9$ in yellow and BaTi$_5$O$_{11}$ in cyan. Raman images of the phase distribution for (b) untreated sample of BaTiO$_3$/TiO$_2$ sample, (c-e) 400°C thermally treated BaTiO$_3$/TiO$_2$ sample and (f) 1000°C thermally treated BaTiO$_3$/TiO$_2$ sample.

From the above discussion, by combining the results of the thermal analysis with the XRD, XPS and CRM analysis the reaction mechanism of BaTi$_5$O$_{11}$ formation through solid-state reaction from core-shell BaTiO$_3$@TiO$_2$ nanoparticles can be schematically illustrated as shown in Figure 7. The first stage portrays the core BaTiO$_3$ raw materials at room temperature obtained by a hydrothermal synthesis in a Segmented Tubular Reactor. BaTiO$_3$ particles possess spherical shape morphology and they form aggregates (corresponding FE-SEM micrographs are included in Supporting Information Figure S2). Raman images show that some
BaTiO$_3$ nanoparticles are carbonated forming BaCO$_3$ at room temperature. In addition, the BaCl$_2$ precursor remains in contact with BaTiO$_3$ particles. Even when the precipitated was carefully washed with water and chloride ions are absent in the supernatant by the silver nitride test method, this compound is found in the BaTiO$_3$ aggregates. The second stage in the scheme illustrates the reaction when an amorphous TiO$_2$ is generated by coating the core BaTiO$_3$ from an aqueous solution of TiOCl$_2$. The presence of the amorphous titania phase produces three main effects: first the elimination of BaCO$_3$; second, through the removal of BaCl$_2$ a rearrangement of the agglomerates; and the amorphization of BaTiO$_3$. XRD and Raman studies expose that BaTiO$_3$ is almost completely decomposed in the presence of amorphous TiO$_2$, which penetrates through the structure of BaTiO$_3$ by the BaCl$_2$ phase. According to the XPS data, it is also evidence that the BaTiO$_3$/TiO$_2$ composite sample presents Ba$^{2+}$ cations at the surface that could be related to the migration of the Ba$^{2+}$ cations during the synthesis process. Thus, an amorphous TiO$_2$ is generated having nucleus of BaTiO$_3$. At the third stage evidence of the crystallization of BaTi$_4$O$_9$ phase appears in presence of amorphous titania. Finally, at 800°C the excess of amorphous TiO$_2$ continues to penetrate the structure and form nanoparticles of the BaTi$_5$O$_{11}$ phase.
Figure 7.- Scheme representing the main stages of the BaTi₅O₁₁ formation. Up-left scheme illustrates the former BaTiO₃ nanoparticle agglomerateas. The next up-right scheme represents the initial reaction between the core-BaTiO₃ aggregates and the peroxotitanium (IV) solution, the final room temperature reaction of the core-shell BaTiO₃/TiO₂ to produce an amorphous Titania with BaTiO₃ rests. The down-right scheme denotes the beginning of the formation of the BaTi₄O₉ particles surrounded by the amorphous Titania phase. Finally, the down-left scheme depicts the formation of the BaTi₅O₁₁ particles.

CONCLUSIONS

In the attempt of obtaining a core-shell structure of TiO₂@BaTiO₃, both the phases evolution and the role of the intermediate compounds during the synthesis of nanostructured BaTi₅O₁₁ have been studied. Core BaTiO₃ particles in form of aggregates present precursor rests as BaCl₂ and local carbonation.
The process of shell formation by an amorphous titania onto core BaTiO$_3$ provokes both the carbonates and the chlorides removal. The progressing of the reaction tooks 10 days and, as the chloride are completely removed, the BaTiO$_3$ particles are chemically attacked by the amorphous titania phase. The thermal treatment of the so obtained materials produces a single phase of BaTi$_5$O$_{11}$. The intermediate phases are identified by a combination of characterization methodologies as Raman Confocal, XRD and XPS. This example shows a strategy to synthesize complex single-phase composition by controlling of the intermediate phase and, in particular, to the residues of the precursors that contributed to the reaction mechanism during the thermal treatment. Finally, the development of BaTi$_5$O$_{11}$ powders is attractive because this material exhibits excellent microwave properties that allow its use in monolithic microwave integrated circuits with reduced particle dimensions.

**SUPPORTING INFORMATION**

Raman spectrum of as obtained core BaTiO$_3$ particles, FESEM micrographs of core BaTiO$_3$ particles, Survey XPS spectrum, Raman spectrum of BaTiO$_3$/TiO$_2$ 400ºC, showing the BaTi$_4$O$_9$ phase.

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We report an effective method to obtain BaTi$_5$O$_{11}$ powder with nanometer-scale crystals. Nanostructured particles consisting of BaTiO$_3$ and TiO$_2$, are used as precursors for the solid-state synthesis of nano BaTi$_5$O$_{11}$ powders at moderate temperatures. The formation mechanisms of BaTi$_5$O$_{11}$ have been explored as a function of temperature and time. The reaction was monitored by Raman spectroscopy combined with Confocal microscopy.