Synthesis of Ferroelectric $Bi_4Ti_3O_{12}$ by Alternative Routes: Wet No-Coprecipitation Chemistry and Mechanochemical Activation

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Novel synthesis methods have been investigated for the preparation of $Bi_4Ti_3O_{12}$ ferroelectric Aurivillius-type powders, namely, the wet no-coprecipitated chemistry using a *n*-butylamine aqueous solution and two mechanochemical activation techniques (vibrating and planetarium mills). For the sake of comparison, $Bi_4Ti_3O_{12}$ powders were also produced by the traditional ceramic route. The syntheses of the crystalline phases were obtained by annealing of the precursors at different temperatures and times. Both the precursors and the thermally treated products were characterized by means of X-ray powder diffraction, thermal analysis, and scanning electron microscopy. The Aurivillius phase was found to appear at 600 °C for vibrating and 500 °C for planetarium-milled precursors. These temperatures are 250−350 °C lower than those reported for the traditional ceramic route (850 °C). Moreover, the stabilization at room temperature of a new fluorite Bi−Ti−O structure was obtained by use of the planetarium milling precursor. The microstructure of the powder investigated by SEM was correlated with the XRD results. In particular, monolithic $Bi_4Ti_3O_{12}$ grains of a few microns in size were achieved by means of the wet chemistry method.

The Aurivillius family of layered perovskite oxides is a group of ferroelectric materials whose properties have been extensively studied. Their crystallographic structures consist of an integer number ("*n*") of perovskite-like units interleaved with $(Bi_2O_2)^{2+}$ layers. The possibility to have lead-free compounds with almost fatigue-free behavior have called the attention of many researchers, especially in the area of thin film technology.[1−7] $Bi_4Ti_3O_{12}$ is a $n = 3$ member of the Aurivillius family of compounds. It has a Curie temperature of 675 °C[8] and a spontaneous polarization as high as 50 μC cm^{-2}. These characteristics together with its high piezoelectric coefficients and low permittivity make it a suitable material for high-temperature transducers, capacitors, and sensors among other applications.

Since the first report for the synthesis of $Bi_4Ti_3O_{12}$ by Aurivillius,[9] its preparation has been mainly performed by the traditional ceramic procedure. This requires temperatures ranging from 850[10,11] to 1100 °C.[9] To decrease the synthesis temperature and to develop more simple preparation protocols, new methods have been proposed. With them chemically derived powders from different kinds of initial reagents by means of coprecipitate[12−15] and sol−gel routes[16] are obtained. Thermal decomposition at 550 °C for 10 min of coprecipitated precursors obtained from Bi_2O_3 and TiO(OH)Cl reagents has been reported as the lowest temperature for $Bi_4Ti_3O_{12}$ Aurivillius preparation.[15] An interesting method consisting of the coprecipitation with 1 M *n*-butylamine stoichiometric aqueous solution (pH ∼ 10.5) produces highly reactive materials. It has been successfully applied for the preparation of well-crystallized spinel-type oxides at low temperatures.[17,18] Nev-

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(1) Auciello, O.; Ramesh, R. (Guest Editors) *MRS Bull.* **1996**, *21*(6−7).

(2) Auciello, O.; Scott J. F.; Ramesh, R. *Phys. Today* **1998**, July, 22.

(3) Pignolet, A.; Welke, S.; Curran, C.; Alexe, M.; Senz, S.; Hesse, D. *Ferroelectrics* **1997**, *202*, 285.

(4) Scott, J. F.; Alexe, M.; Zakharov, N. D.; Pignolet, A.; Curran, C.; Hesse, D. *Integr. Ferroelectr.* **1998**, *21*, 1.

(5) Pintilie, L.; Alexe, M.; Pignolet, A.; Hesse, D. *Appl. Phys. Lett.* **1998**, *73*, 342.

(6) Alexe, M.; Scott, J. F.; Curran, C.; Zakharov, N. D.; Hesse, D.; Pignolet, A. *Appl. Phys. Lett.* **1998**, *73*, 1592.

(7) Switzer, J. A.; Shumsky, M. G.; Bohannan, E. W. *Science* **1999**, *284*, 293.

(8) Fouskova, A.; Cross, L. E. *J. Appl. Phys.* **1970**, *41*, 3834.

(9) Aurivillius, B. *Arkiv Kem.* **1949**, *1*, 499.

(10) Huanosta, A.; Álvarez-Fregosos, O.; Amano, E.; Tabares-Muñoz, C.; Mendoza-Álvarez, M. E.; Mendoza-Álvarez, J. G. *J. Appl. Phys.* **1991**, *69*, 404.

(11) Hervoches, C. H.; Lightfoot, P. *Chem. Mater.* **1999**, *11*, 3359.

(12) Jovalekic, C.; Stevic, S. *Ferroelectrics* **1992**, *132*, 185.

(13) Villegas, M.; Moure, C.; Fernández, J. F.; Durán, P. *J. Mater. Sci.* **1996**, *31*, 949.

(14) Jiang, A. Q.; Li, G. H.; Zhang, L. D. *J. Appl. Phys.* **1998**, *83*, 4878.

(15) Horn, J. A.; Zhang, S. C.; Selvaraj, U.; Messing G.; Trolier-McKinstry, S. *J. Am. Ceram. Soc.* **1999**, *82*, 921.

(16) Soares-Carvalho, F.; Thomas, P.; Mercurio, J. P.; Frit, B. *J. Sol−Gel Sci. Technol.* **1997**, *8*, 759.

(17) Vila, E.; Rojas, R. M.; Martín de Vidales, J. L.; García-Martínez, O. *Chem. Mater.* **1996**, *8*, 1078.

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ertheless, it has never been tested for the preparation of any Aurivillius-like compounds.

The novel mechanochemical activation technique consists of the energetic milling of the initial stoichiometric powder mixture until a nanocrystalline, amorphous, and mechanochemical activated compound is obtained. The energy transfer to the powder takes place by a shearing action or impact of the high-velocity balls with the powder. The crystallographic structure is completely damaged and the size of the powder reduced by impact. Hence, this process allows enhancement of the kinetics of compound formation and crystallographic phase transformation by means of the high reactivity of the milled powders. In fact, it has been demonstrated that by means of thermal annealing of these activated precursors, it is possible to obtain the materials at lower temperatures and reaction times with respect to the traditional ceramic process. In particular, it has been applied for intermetallic alloy[19] and only recently for Aurivillius-type compounds.[20,21]

This paper deals with the preparation of $Bi_4Ti_3O_{12}$ by innovative routes, different from the traditional ceramic procedure. The used methods were the mechanochemical activation and a wet chemical procedure where the precursors are obtained by precipitation with *n*-butylamine aqueous solution. It will be demonstrated that by these methods the synthesis protocol of the bismuth titanium oxide is largely improved with respect to the traditional ceramic procedure.

Experimental Procedure

Three different procedures have been applied to synthesize $Bi_4Ti_3O_{12}$ ceramics. They were the classical solid-state reaction and the *n*-butylamine and mechanochemical activation methods. In the latter case, the vibrating and planetarium mills were used. The powders obtained by the different procedures were subjected to different thermal annealing processes in air at temperatures of 300 °C and higher.

In the case of the *n*-butylamine procedure, the $Bi_4Ti_3O_{12}$ precursor was prepared by adding the amount of TiO_2 (Merck, analytical grade) required to obtain a Bi:Ti molar ratio of 4:3 to 0.04 mol of $Bi(NO_3)_3{\cdot}5H_2O$ dissolved in 300 mL of distilled water, under continuous stirring. The precursor material was obtained after 1 h of precipitation of Bi^{3+} cation with 1 M solution of *n*-butylamine ($pH \sim 10.5$) at room temperature. The solid prepared in this manner is formed by a physical mixture of the anatase (TiO_2) and the amorphous $Bi_2O_3{\cdot}nH_2O$. Then, this mixture was washed with distillate water, centrifuged, and dried at 80 °C overnight. A detailed description of the synthesis procedure was published elsewhere.[22]

For the traditional and milling procedures, the stoichiometric mixture of Bi_2O_3 and TiO_2 (both analytical grades) was initially homogenized by hand in an agate mortar. In the traditional ceramic route, the material was treated at increasing temperatures from 500 to 800 °C with intermediate regrinding steps. The powder was maintained at each temperature for 12 h. For the mechanochemical activation, the vibrating and planetarium mills (Fritsch, models Pulverizette 0 and 6) were used. In both cases, the initial oxide mixture was placed in a stainless steel pot with balls of the same material. In the vibrating mill one ball of 5-cm diameter was used, whereas in the planetarium mill five balls of 1-cm diameter each were utilized. In the vibrating mill the powder was ground from 1 to 168 h. For the planetarium, the grinding bowl was rotated at 200 rpm. The ball:powder weight ratio was about 16:1. The grinding time ranged from 1 to 72 h.

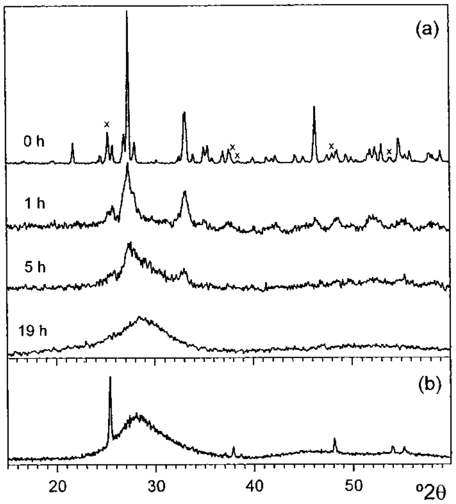

Figure 1. XRD recording taken at room temperature of a (a) $4Bi_2O_3{:}3TiO_2$ oxide mixture after different milling times. The grinding was carried out by a planetarium mill; (b) precursor obtained in the *n*-butylamine method (×, TiO_2 (anatase)).

The powders were characterized by X-ray powder diffraction (XRD) at room and increasing temperatures, differential thermal analysis (DTA), thermogravimetry (TG), and scanning electron microscopy (SEM). XRD recordings at room temperature were performed with scan rates of 0.05° (2θ) per second (Siemens D500). At higher temperatures, XRD studies were carried out in a heating chamber (Anton Paar HTK10) depositing a small quantity of powder onto a platinum sheet, which acts as the heating element. In that case the scans were taken at rates of 0.02° (2θ) per second (Philips PW1710). The temperature was monitored by a Pt−Pt 13% Rh thermocouple welded onto the center of the platinum sheet. The heating rate was 10 °C min^{-1}. Care was taken to stabilize the temperature before the measurement. All the diffractograms were acquired using Cu Kα radiation ($\lambda = 0.15418$ nm). DTA and TG investigations were carried out at 10 °C min^{-1} heating/cooling rates from room temperature to 1100 °C in air (Seiko 320). About 10-mg samples were used and α-Al_2O_3 was the inert reference material. To perform SEM measurements (Philips SFEG-XL30 model), suspensions of the powders in ethanol were precipitated on a smooth silicon surface. No additional gold layer was sputtered on. Images were taken at 3 and 5 kV, depending on the charging of the samples. To obtain a high-resolution image of the surface topography, a through-the-lens-detector mode was used.

In the following, the powders used for the thermal analysis and heating treatments will be referred to as the initial precursors.

Results and Discussion

Initial Precursors. In both milling processes, the oxides progressively lose their crystalline characteristics as a function of the grinding time (Figure 1a). Initially, the XRD recordings displayed the whole set of well-defined peaks associated with the crystalline mixture of oxides. After a few hours these signals became significantly broadened and less intense. Finally, the diffractogram is formed by only one maximum with a few degrees in width. In the vibrating mill, the amorphous aspect is obtained after 168 h (not shown here). This time is reduced to 19 h for the case of the

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(18) López-Delgado, A.; Martín de Vidales, J. L.; Vila, E.; López, F. A. *J. Alloys Compd.* **1998**, *281*, 312.

(19) Murty, B. S.; Ranganathan, S. *Int. Mater. Rev.* **1998**, *43*, 101.

(20) Castro, A.; Millán, P.; Pardo, L.; Jiménez, B. *J. Mater. Chem.* **1999**, *9*, 1313.

(21) Castro, A.; Millán, P.; Ricote, J.; Pardo, L. *J. Mater. Chem.* **2000**, *10*, 767.

(22) Martín de Vidales, J. L.; Rojas, R. M.; Vila, E.; García-Martínez, O. *Mater. Res. Bull.* **1994**, *29*, 1163.

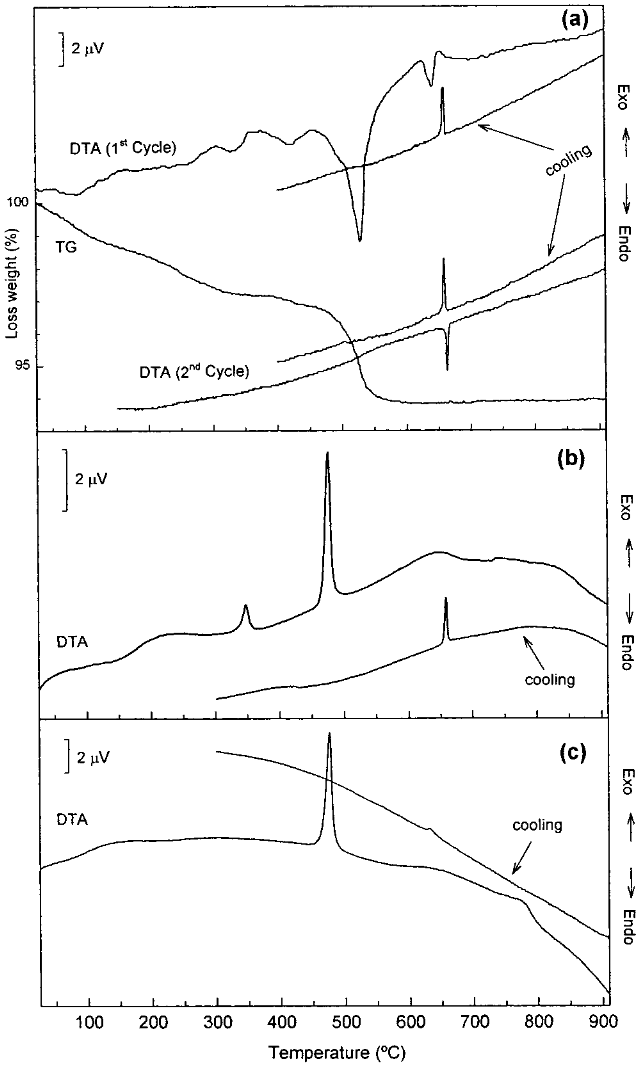

Figure 2. DTA curves of (a) the *n*-butylamine precursor and the amorphous ones obtained from (b) vibrating ball (168 h) and (c) planetarium mills (72 h). TG curve and two cooling/heating cycles are also shown in (a).

planetarium (Figure 1a). It is important to note that these thereby prepared precursors are completely different from the highly crystalline ones, which are used in the traditional ceramic route (see Figure 1a, 0 h). The loss of crystallinity is caused by the energetic milling process.

In the *n*-butylamine method, the amorphous broad band overlapped with the TiO_2 (anatase) diffraction lines. This observation suggests that, during the obtaining of the precursor, the crystalline TiO_2 structure is not affected. The halo corresponds to the bismuth components ($Bi_2O_3 \cdot nH_2O$) (Figure 1b).

Thermal Behavior. Figure 2a depicts the thermal analysis curves acquired from two consecutive heating/cooling cycles in the case of the precursors obtained in the *n*-butylamine method. TG tracing shows variations in the first heating cycle between room temperature and 550 °C. The experimental mass loss of $\approx$6 wt % is caused by the thermal removal of water, nitrates, and organic ions adsorbed on the solid particles. For the next cooling–heating–cooling processes the TG curve was constant (not shown in Figure 2a). In the case of milling procedures no weight change during the whole set of heating/cooling cycles was observed.

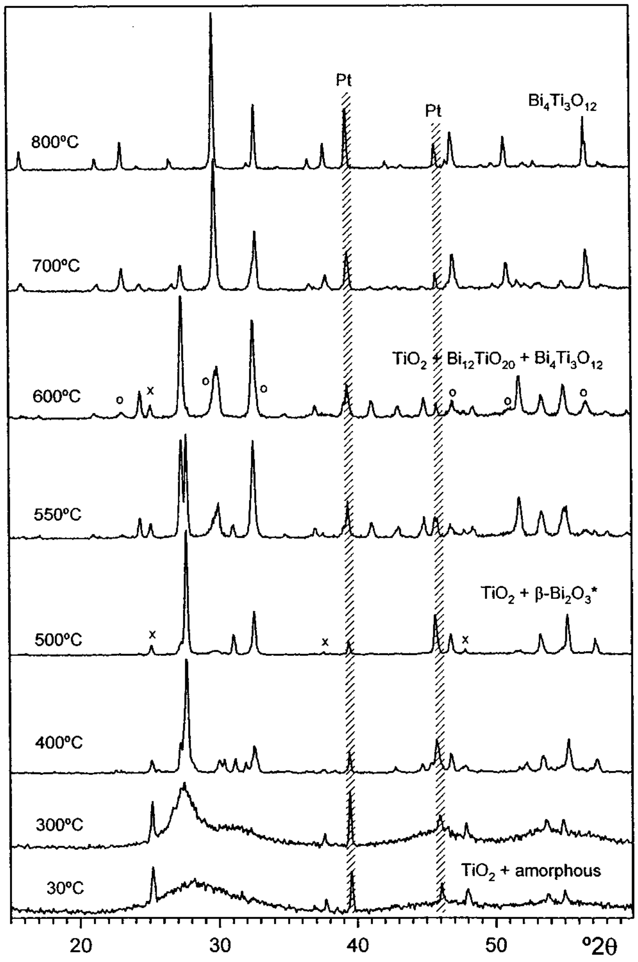

Figure 3. XRD high-temperature patterns recorded for the *n*-butylamine precursor (×, TiO_2; ○, $Bi_4Ti_3O_{12}$; dashed lines, Pt (sample holder); *, β-Bi_2O_3 is partially doped).

DTA curves displayed interesting features in the first heating cycle. The precursor obtained from the *n*-butylamine process exhibited several endothermic peaks between room temperature and 655 °C (Figure 2a) whereas in the milling methods only exothermic maximums were observed (Figure 2b,c). The vibrating ball-milling precursor (168 h) showed two sharp peaks at 349 and 476 °C (Figure 2b). In the planetarium mill the number of peaks depended on the grinding time. At 19 h the results were similar to those obtained with the vibrating system. The exothermic effects appeared at 381 and 475 °C. Nevertheless, at 72 h only one exothermic peak at 474 °C was measured (Figure 2c).

For the next cooling–heating–cooling cycles the results are quite similar for the whole set of samples, independent of the precursors used (see Figure 2a). One endothermic peak upon heating (637–664 °C) and one exothermic peak upon cooling (630–660 °C) were measured. They might be related to the reversible para-ferroelectric transition of the $Bi_4Ti_3O_{12}$ Aurivillius material ($T_C = 675$ °C[8]).

Interpretations of the DTA and TG recordings for the first heating process were made on the basis of XRD taken at increasing temperatures (Figures 3 and 4). The initial amorphous band of the *n*-butylamine precursor became narrower as the temperature increased (Figure 3). Hence, at 500 °C was identified a compound that could be either β-Bi_2O_3 (JCPDS 27-50) or $Bi_{20}TiO_{32}$

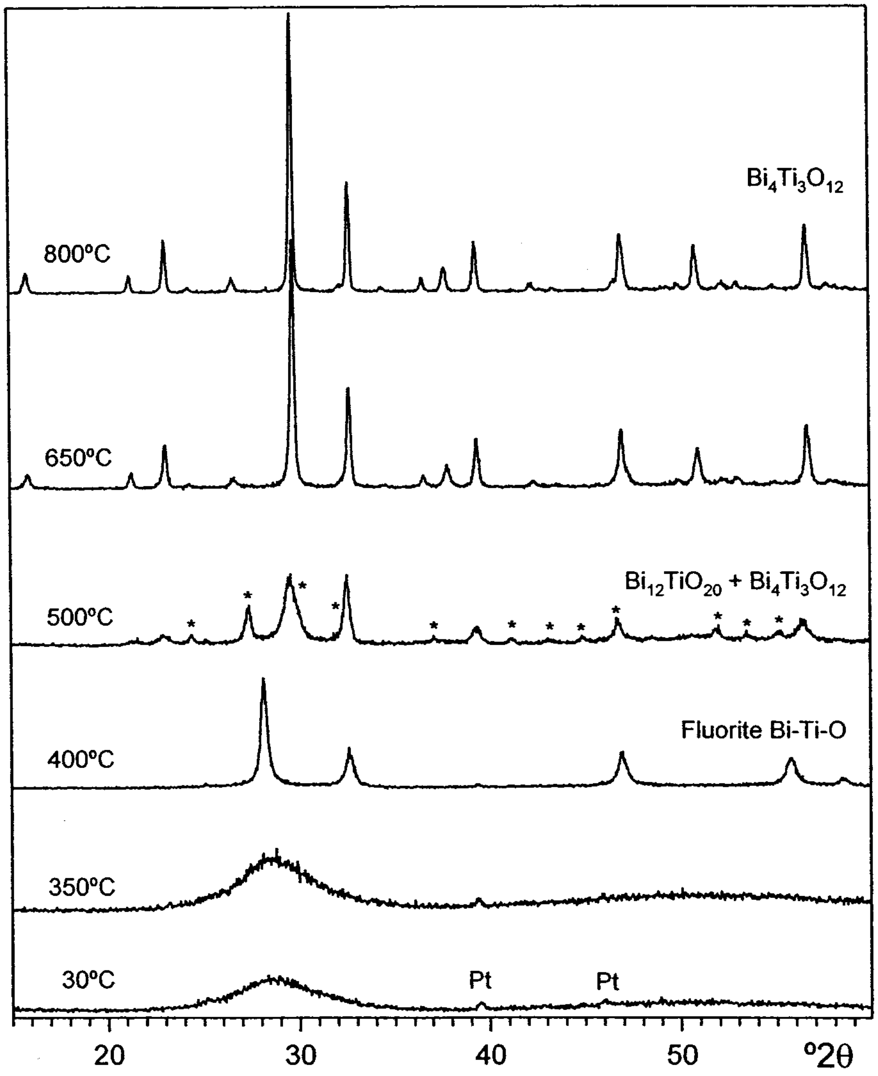

Figure 4. XRD recordings taken at increasing temperatures of the planetarium milling precursor (19 h of mechanical grinding; *, $Bi_{12}TiO_{20}$).

(JCPDS 42-202). Because of the similarity of both diffraction patterns, and the slight shift of the recorded peaks caused by the thermal expansion of the samples, it is not possible to ensure which phases form this diffractogram. This crystallographic transformation is assigned to the endothermic peak observed between 380 and 450 °C. Beyond this temperature, at 600 °C the XRD recording was formed mainly by $Bi_{12}TiO_{20}$ (JCPDS 34-97) and small quantities of TiO_2 and $Bi_4Ti_3O_{12}$. This is correlated with the endothermic processes in the DTA curve observed between 475 and 575 °C where two peaks are overlapped with position at 500 and 535 °C (Figure 2a). The former peak, which appears as a shoulder, corresponds to the loss of weight shown in the TG recording. According to this observation, it is concluded that the endothermic peak in the DTA curve at 535 °C corresponds to the formation of $Bi_{12}TiO_{20}$. The last endothermic maximum at 640 °C is related to the $Bi_4Ti_3O_{12}$ Aurivillius phase crystallization. Actually, at 700 °C the Aurivillius phase is predominant; however, traces of the $Bi_{12}TiO_{20}$ phase are still present. The Aurivillius compound is found as a single phase at 800 °C (Figure 3).

In the case of vibrating ball-milling precursors, XRD confirms the presence of the amorphous material until the first exothermic peak is observed at 349 °C. This peak corresponds to the formation of a fluorite-like Bi−Ti−O compound, like that previously reported for Bi_3TiNbO_9.[20] The formation of the Bi−Ti−O fluorite is accompanied by a parasite phase that has not been identified. The DTA exothermic peak at the highest temperature (476 °C) is correlated with the formation of the $Bi_{12}TiO_{20}$ and $Bi_4Ti_3O_{12}$ phases, similar to that observed in the *n*-butylamine process aforementioned. $Bi_4Ti_3O_{12}$ is obtained as a pure phase at 600 °C.

Thermal behavior of the planetarium samples ground for 19 h (Figure 4) was quite similar to the vibrating ball-milling powders. The DTA exothermic peak observed at the lowest temperature (381 °C) corresponds to the crystallization of a fluorite Bi−Ti−O structure. In that case the fluorite phase can be entirely isolated. At the highest temperature (475 °C) the fluorite is transformed into $Bi_4Ti_3O_{12}$ and $Bi_{12}TiO_{20}$. The Aurivillius phase is obtained in this case as a pure phase at 650 °C (Figure 4). The most different thermal behavior is observed in the planetarium sample ground for 72 h. In that case the unique exothermic DTA peak detected (476 °C) corresponds to the amorphous to Aurivillius phase transition without the presence of any other intermediate phase.

Table 1. Annealing Conditions Used in Furnace Treatments for the Precursors Obtained in the *n*-Butylamine and Milling Procedures (RT = room temperature, M = initial mixture oxide $4Bi_2O_3{:}3TiO_2$, A = Amorphous, F = Fluorite, lc = Low Crystallinity)

Treatment T °C/t h	n-butylamine precursor
RT	TiO_2 + A (bismuth components)
300 / 1	TiO_2 + bismuth oxides (not identified)
450 / 1	TiO_2 + β-Bi_2O_3* (partially doped)
500 / 1	TiO_2 + β-Bi_2O_3* + $Bi_{12}TiO_{20}$
520 /1	TiO_2 + $Bi_{12}TiO_{20}$
600 / 1	TiO_2 + $Bi_{12}TiO_{20}$ + $Bi_4Ti_3O_{12}$
750 / 1	$Bi_4Ti_3O_{12}$

	Milling precursors		
	Milling time (h)		
	Vibrating ball milling		
	0	72	168
RT	M	M + A	A
500 / 12	M	F + $Bi_4Ti_3O_{12}$	F + $Bi_4Ti_3O_{12}$
600 / 3	-	$Bi_4Ti_3O_{12}$ + F	$Bi_4Ti_3O_{12}$
600 /12	$Bi_4Ti_3O_{12}$ + $Bi_{12}TiO_{20}$	$Bi_4Ti_3O_{12}$	
700 / 12	$Bi_{12}TiO_{20}$ + $Bi_4Ti_3O_{12}$		
800 / 12	$Bi_{12}TiO_{20}$+ $Bi_4Ti_3O_{12}$		
850/ 12	$Bi_4Ti_3O_{12}$		

	Planetarium milling	
	19	72
RT	A	A
350 / 1	F	-
400 / 1	$Bi_4Ti_3O_{12}$ + F + $Bi_{12}TiO_{20}$	A
460 / 3	-	$Bi_4Ti_3O_{12}$ (lc)
500 / 1	$Bi_{12}TiO_{20}$ + $Bi_4Ti_3O_{12}$	$Bi_4Ti_3O_{12}$ (lc)
550 / 1	$Bi_{12}TiO_{20}$ + $Bi_4Ti_3O_{12}$	$Bi_4Ti_3O_{12}$
600 / 1	$Bi_4Ti_3O_{12}$	

To isolate each stable phase at room temperature, the precursors were heated in a furnace at similar temperatures as those used in the high-temperature XRD technique and then were quenched in air. The crystallographic transformations were analogous to those aforementioned, although the synthesis temperatures were between 50 and 100 °C lower. A summary of the compounds obtained in the different thermal treatments is given in Table 1 for the whole set of precursors studied.

Major differences were observed in the *n*-butylamine method. In that case, at 300 °C appeared a series of diffraction peaks, which may be associated with different kinds of bismuth compounds. These phases could not be identified. At 450 °C the diffractograms were mainly formed by TiO_2 and β-Bi_2O_3. However, the peak positions of the bismuth oxide were slightly shifted. This observation suggests that the bismuth oxide is partially doped with titanium atoms forming in the intermediate phase between β-Bi_2O_3 and $Bi_{20}TiO_{32}$. At temperatures as high as 520 °C all bismuth was present, forming $Bi_{12}TiO_{20}$, whereas the Aurivillius compound was observed as a single phase at 750 °C.

It is important to mention that, in the case of powders synthesized by means of the traditional ceramic route, $Bi_{12}TiO_{20}$ was also observed as an intermediate compound in the formation of the Aurivillius phase. From 500 to 800 °C both phases were present, decreasing the intensities of the $Bi_{12}TiO_{20}$ phase as the temperature increased. $Bi_4Ti_3O_{12}$ is only isolated at 850 °C.

Morphological Characterization. Mechanochemical Activated Powders. The initial oxide powders used in the milling procedures consisted mainly of spherical particles with diameters between 50 and 200 nm (Figure 5a). There was also a small fraction of larger grains characterized by flat surfaces with diameters ranging from 0.5 to 5 μm. These two grain types show the coexistence of the two oxide initial phases (Bi_2O_3 and TiO_2). TiO_2 particles correspond to the smaller grains (Figure 5a).

The major change in the morphology after 168 h of vibrating ball milling is the disappearing of the large grains with respect to the initial powders (Figure 5b). Additionally, the size distribution of the smaller grains is slightly wider, ranging from 50 to 350 nm. They have less spherical shape and seem to be more agglomerated.

In comparison to vibrating ball milling, the morphology is much more affected in the planetarium, even at short milling times. At 19 h the powders are constituted by large agglomerates a few microns in size. They have

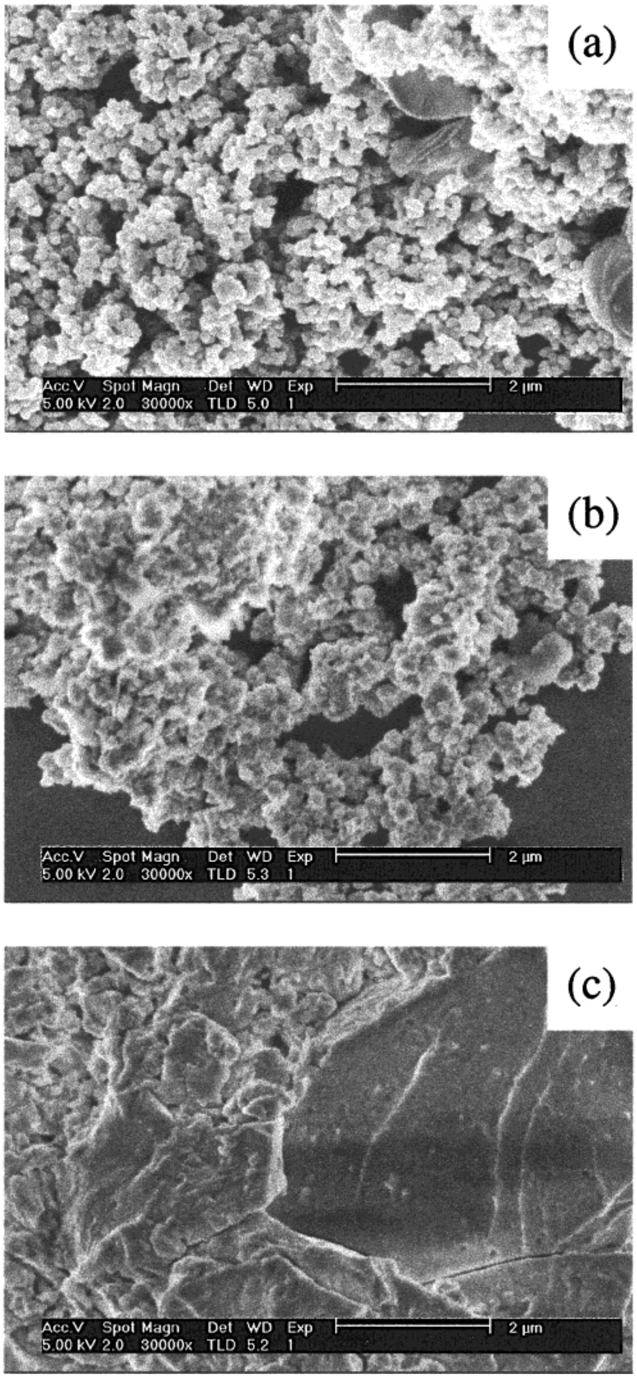

Figure 5. Scanning electron micrographies of (a) the initial $4Bi_2O_3$:$3TiO_2$ oxide mixture, (b) vibrating ball milling (168 h), and (c) planetarium (72 h) amorphous precursors.

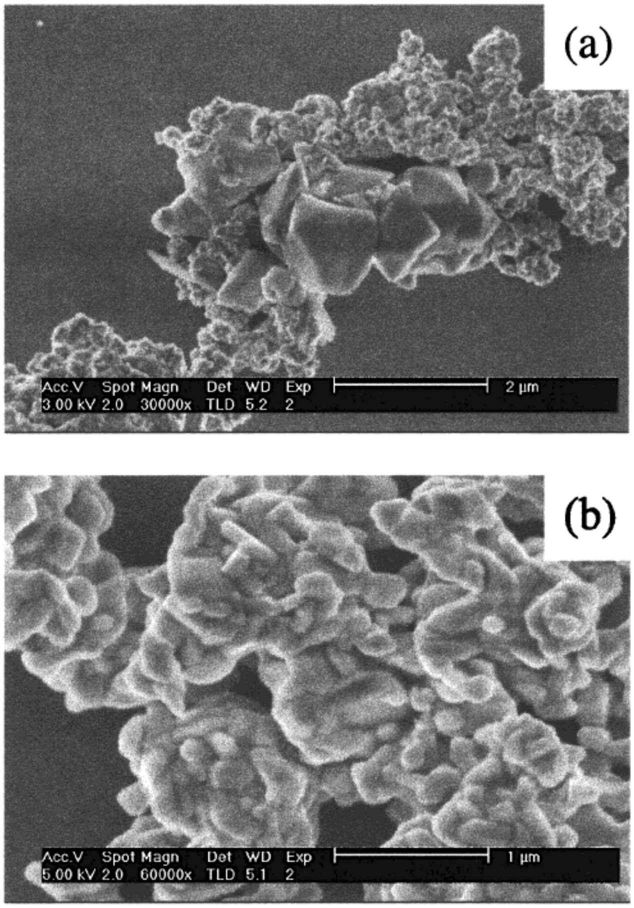

Figure 6. Scanning electron micrographies of the vibrating ball-milling precursor annealed at (a) 500 °C for 12 h (Bi−Ti−O fluorite) and (b) 600 °C for 3 h ($Bi_4Ti_3O_{12}$ Aurivillius phase).

irregular shapes and are formed by the coalescence of small grains. The trend to coalesce is even stronger at 72 h of milling (Figure 5c). In this case the large particles exhibit partially smoother surfaces where no smaller grains can be distinguished. In addition, some of the larger particles appear like unique grains.

Because of annealing, there are changes in the morphology of the samples. In comparison to the untreated precursors to a thermally treated vibrating ball-milling powder (500 °C/12 h), the main difference is the appearance of large faceted grains with a pronounced crystal habit (Figure 6a). The habit indicates cubic symmetry and therefore may be related to the fluorite-like Bi−Ti−O phase detected by XRD. However, there remains a portion of material formed by small grains similar to those observed in the untreated sample. These results suggest that the formation of the fluorite is not complete and the parasite phase observed by XRD may be related to the smaller particles.

In contrast to the previous results, the overall morphology is changed when treatments of 600 °C for 3 h are carried out with vibrating ball-milling precursors (Figure 6b). In this case a unique type of crystals with anisotropic habit can be seen, typically observed in $Bi_4Ti_3O_{12}$ Aurivillius ceramics. This result suggests that there is a complete phase transition from the initial amorphous to the crystalline $Bi_4Ti_3O_{12}$ Aurivillius phase (Figure 6b). In general, there is a trend to increase grain size with respect to the initially amorphous precursors.

For planetarium milling samples (19 h) a treatment of 350 °C for 1 h does not affect the morphology of the initial precursor (Figure 7a). A combination of this result with that obtained in the XRD measurements, where a transition to the fluorite-like Bi−Ti−O structure was observed, leads to the conclusion that the crystallization process involves only reorganization on a scale smaller than the grain size. The morphology of the Aurivillius $Bi_4Ti_3O_{12}$ powders obtained at 600 °C for 1 h shows differences as a function of the milling time, 19 and 72 h, respectively (Figure 7b,c). In the former case two different grain types are observed: platelike crystals typical for the Aurivillius phase as aforementioned and agglomerates of smaller grains. For the latter, ag-

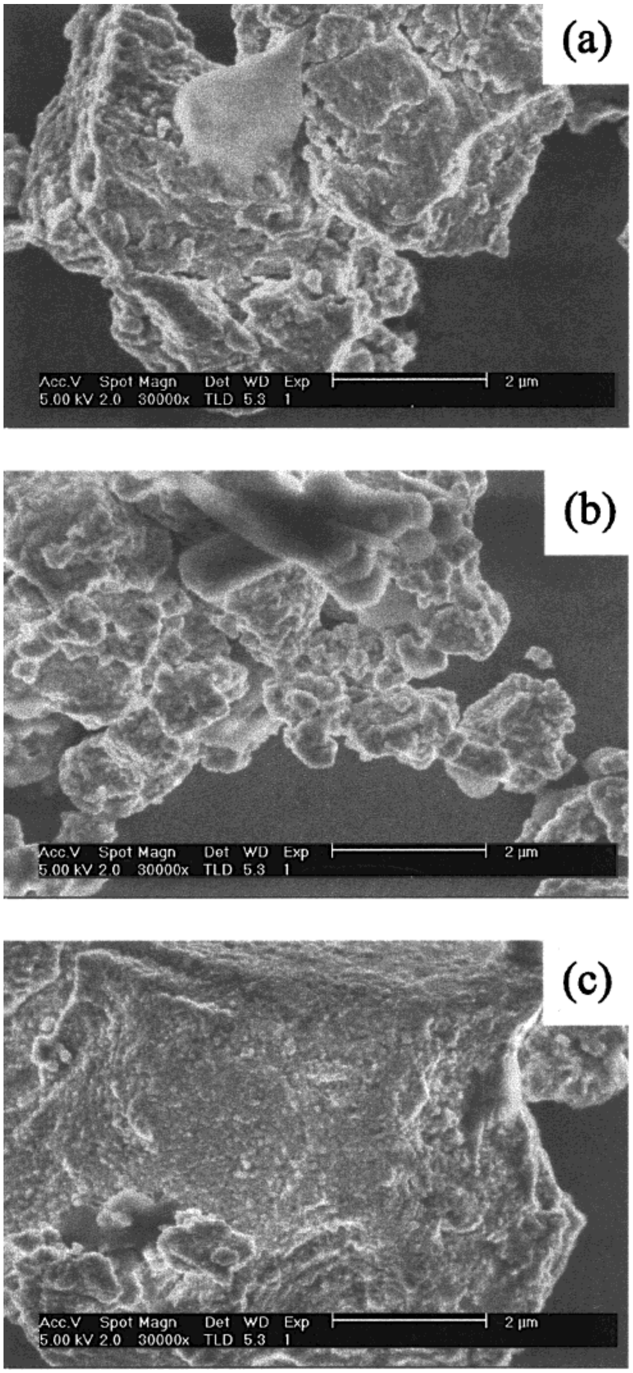

Figure 7. Scanning electron micrographs of (a) Bi−Ti−O fluorite obtained from the planetarium precursor (19 h) treated at 350 °C for 1 h. (b) and (c) correspond to $Bi_4Ti_3O_{12}$ Aurivillius powders attained at 600 °C for 1 h. The precursors were mechanoactivated with the planetarium mill for 19 and 72 h, respectively.

glomerates of a unique grain type are observed. Their surface is rougher in comparison to the amorphous reagent (Figure 5c). This different behavior is not well understood at the moment. One may speculate that the growth of $Bi_4Ti_3O_{12}$ large grains is related to a less intimate mixture of the initial oxide powder. However, the difference observed here may allow a certain control of grain sizes by choosing an adequate milling time.

***n*-Butylamine Method.** The initial precursor exhibits one kind of particles with smooth surfaces that indicate that both compounds (TiO_2 and $Bi_2O_3{\cdot}nH_2O$) do not separate in different grain types, having intimate contact (Figure 8a).

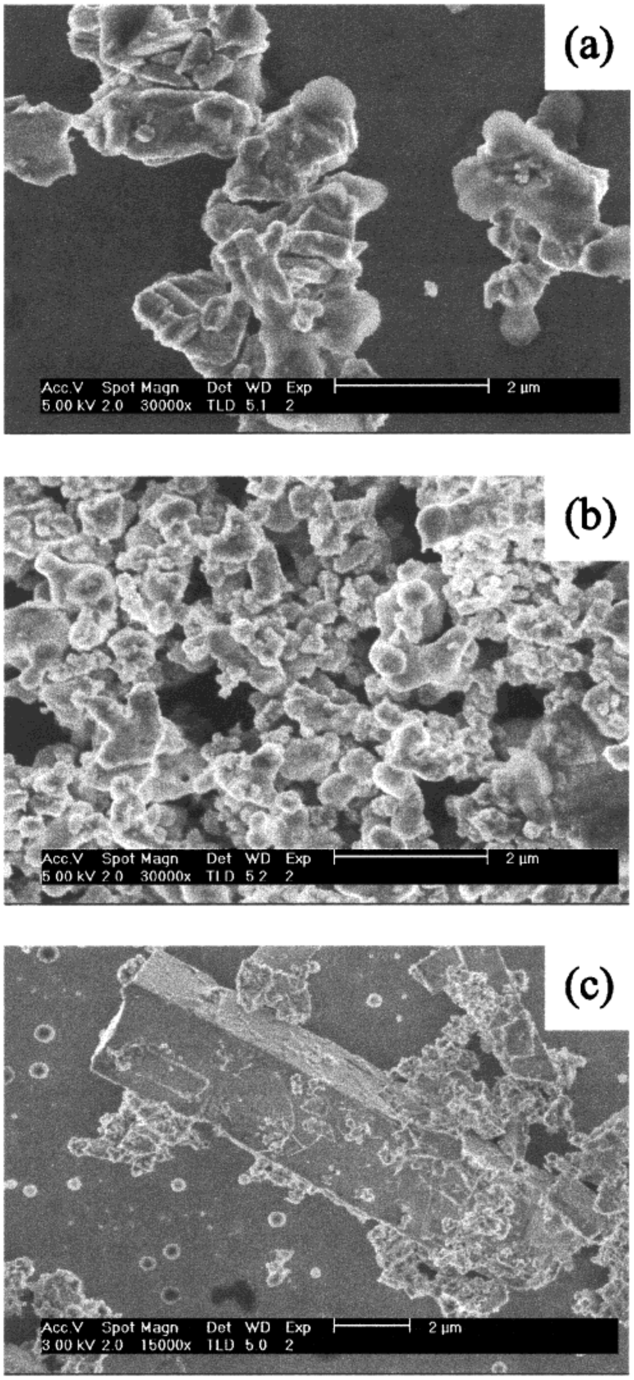

Figure 8. Scanning electron micrographs of (a) *n*-butylamine precursor and treated at (b) 520 °C for 1 h ($Bi_{12}TiO_{20}$) and (c) 750 °C for 1 h ($Bi_4Ti_3O_{12}$).

With treatment of 520 °C for 1 h the particles are smaller and rounder in comparison to those of the initial reagent. The presence of the smaller grains (approximately hundreds of nanometers in size) indicates that during thermal treatment the initial present particles have partially separated into smaller ones. They may correspond to the $Bi_{12}TiO_{20}$ phase formation observed by XRD (Figure 8b).

As the temperature increases and the Aurivillius $Bi_4Ti_3O_{12}$ phase is obtained (750 °C for 1 h), the morphology is characterized by a broad grain size distribution ranging from a few tens of nanometers to micrometers.

In particular, large grains with a clear monolithic crystal habit with anisotropyc shapes are observed, the long axis reaching some micrometers (Figure 8c). It is interesting to note that this monolithic shape with these kinds of dimensions was not observed both in the mechanochemical activated routes and in the traditional ceramic procedure.

Conclusions

The formation of $Bi_4Ti_3O_{12}$ Aurivillius phase has been achieved by using different precursors obtained from *n*-butylamine and mechanoactivated routes.

The *n*-butylamine method is presented as a no-coprecipitated route. During the formation of the precursor only the bismuth components are dissolved and the TiO_2 particles are maintained unaltered. This result is in agreement with the phase stability diagram of TiO_2 in water at different pH conditions calculated by Eckert et al.[23] They show that at pH $\sim$ 10 only a small amount of the TiO_2 (anatase) is hydrolyzed and the equilibrium molality is about 10^{-7} at 90 °C. Anatase is stable in alkaline aqueous solutions.

The presence of $Bi_{12}TiO_{20}$ as an intermediate compound might be related to less homogeneous compositions in the ground precursors. In fact, when the energetic mechanical milling by planetarium is carried out, during a proper period of time (72 h), this $Bi_{12}TiO_{20}$ phase is no longer observed. On the other hand, the occurrence of Ti-poor phases in the *n*-butylamine method seems to be more related to the crystallization process in the obtaining of $Bi_4Ti_3O_{12}$. Crystallographic evolution as a function of the annealing temperatures indicates that the initial bismuth amorphous components incorporate the titanium ones in different progressive amounts. This allows the formation of metastable Ti-poor phases that finally approach the stable stoichiometric equilibrium $Bi_4Ti_3O_{12}$ Aurivillius material.

Planetarium milling allows isolation of a Bi−Ti−O fluorite, never observed by classical reaction methods. Because of the lack of morphological changes between the initial precursor and the fluorite, it suggests that this fluorite is directly synthesized during the mechanical activation as nanosized crystallites.

Mechanoactivation produces a lowering of about 300 °C in the $Bi_4Ti_3O_{12}$ formation with respect to the traditional ceramic procedures (850 °C). This is a consequence of the high internal energy of the ground particles caused by the defects generated during milling. The morphologies of the Aurivillius compounds show that the *n*-butylamine and milling methods would enable the preparation of ceramics with different mechanical, dielectric, ad ferroelectric characteristics by controlling the crystal habit and grain sizes.

The simple protocols and the useless hazardous reagents make these three methods here proposed very promising.

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(23) Eckert, J. O.; Hung-Houston, C. C.; Gersten, B. L.; Lencka, M. M.; Riman, R. E.; *J. Am. Ceram. Soc.* **1996**, *79*, 2929.