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Synthesis of the Aurivillius Phase $SrBi_4Ti_4O_{15}$ by a Mechanochemical Activation Route

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This work reports the results obtained on the synthesis of the Aurivillius oxide $SrBi_4Ti_4O_{15}$ as carried out by mechanochemically assisted methods. The effects of changing the milling media (vibrating and planetary mills) and the length of the mechanical treatment are discussed. The products obtained were characterized by X-ray diffraction at room and high temperatures, thermal analysis, and scanning electron microscopy. When an amorphous mechanochemically activated precursor is annealed at low temperatures, a novel Sr−Bi−Ti−O fluorite-related phase is isolated. The bismuth layered perovskite can be obtained with a significant decrease in temperature (of about 500 °C) and reaction time (several days), as compared with the conventional ceramic synthesis method. The mechanically treated samples exhibit a homogeneous particle size of around 300 nm, which increases with further thermal annealing.

Introduction

The Aurivillius family (A'_2O_2) $(A_{n-1}B_nX_{3n+1})$[1] of layered oxides is well-known for the important ferroelectric behavior at high temperatures of some of its terms (Curie temperature above 500 °C in many of them).[2,3] It is expected that some of its members may become substitutes for the leading ferroelectric material, lead zirconate titanate (PZT), whose good ferroelectric properties are counterbalanced by an excessive toxicity due to its high lead content.[4] Lead-free $SrBi_2Ta_2O_9$[5] and $Bi_4Ti_3O_{12}$[1] could qualify as candidates to do the job, but low remanent polarization in the first and ferroelectric fatigue in the second are serious inconveniences.[6,7] We have investigated the layered bismuth phase $SrBi_4Ti_4O_{15}$, for which some data have been published recently.[8,9]

The framework of the Aurivillius structure type can be described as formed by two different blocks of the form $(A'_2O_2)^{2+}$ and $(A_{n-1}B_nX_{3n+1})^{2-}$ stacked along the *c*-axis in the crystal structure.[1] The (A'_2O_2) slabs belong to the red-PbO structure type; A′ is generally the cation Bi^{III}, in some occasions partially substituted for by Te^{IV}, Pb^{II}, Sb^{III},[10−12] and other ions characterized by having a lone pair of electrons.[13] The $(A_{n-1}B_nX_{3n+1})$ block has a pseudo-perovskite structure, where A is a large cation having coordination number 12, such as Bi^{III}, Ca^{II}, Ba^{II}, Sr^{II}, Ln^{III} (Ln = Lanthanide ion), etc.,[5,14,15] and B is an octahedrally coordinated cation such as Ti^{IV}, Ta^{V}, Fe^{III}, W^{VI}, etc.;[16−18] X usually is O, in rare occasions[19] partially substituted for by F, so the formula is generally given as $A_{n-1}B_nO_{3n+1}$, where *n* is the number of BO_6 octahedra linking the (A'_2O_2) layers.

Aurivillius phases have, to date, been prepared by conventional solid-state methods, a procedure requiring long reaction times and high temperatures, and involving serious problems, such as stoichiometry losses and uncontrolled particle size. To avoid these problems, mechanochemical activation has been tried. Mechanochemically assisted preparation is a novel technique in which mechanical energy is supplied to the starting products by means of vigorous ball milling.[20,21] In some cases, a homogeneous powder is obtained,[22] which appears to XRD as an amorphous precursor, where the grain size is of the order of the nanometer, and the defects and the disorder in the sample have increased,

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so that the specific surface is large, and there is a corresponding decrease of the activation barrier, thus favoring chemical reactions.[21] These factors make the temperature and reaction times decrease, leading to smaller losses of stoichiometry. The powder is then said to be mechanically activated and its high reactivity favors processing, with improvement in the electrical properties.[23−25] In other cases, the powder obtained can be a crystalline pure phase material,[26,27] and the process is then properly called mechanosynthesis.

A prior attempt at the preparation of $SrBi_4Ti_4O_{15}$ ($n = 4$) by a mechanochemically activated route has recently been made,[28] and mechanosynthesis of the mixed oxide was reported, but the product exhibited very poor crystallinity. In this paper we report on the preparation of this material by mechanochemically assisted methods, for which we always obtain an amorphous, very reactive phase, which can be thermally treated to full crystallinity. The effects of changing the milling technique and the milling times of treatment are studied.

Experimental Section

The synthesis of $SrBi_4Ti_4O_{15}$ has been carried out by two different procedures, ceramic route and mechanochemical activation. The initial products are the same for the two methods: Bi_2O_3 (Cerac, 99.9% pure), TiO_2 (anatase, Cerac, 99.5% pure), and $SrCO_3$ (Cerac, 99.9% pure). These were homogenized by hand in an agate mortar, in stoichiometric proportions, to obtain 3 g of $SrBi_4Ti_4O_{15}$.

The conventional solid-state reaction method requires cumulative treatment for the Aurivillius phase to be obtained. The heating sequence is 12 h each at 800, 900, 1000, and 1050 °C, with hand homogenization and characterization by X-ray powder diffraction (XRD) at room temperature after each successive step.

Stainless steel vessels and balls were used for mechanical activation in vibrating and planetary mills (Fritsch, Pulverizette models 0 and 6, respectively; the planetary mill was operated at 200 rpm). The vibrating mill uses one 5-cm-diameter ball and the planetary mill uses five 1-cm balls. The sample evolution under mechanical treatment was followed by XRD according to the protocol shown in Table 1.

The mechanically treated samples were characterized by X-ray powder diffraction (XRD) at increasing temperatures, recorded with a Philips PW1710 diffractometer fitted with an Anton Paar HTK 10 attachment to stabilize the temperature during the measurements. The temperature was monitored by a Pt−Pt 13% Rh thermocouple welded onto the center of the platinum sample holder. The temperature was stabilized for 30 min before the measurement of the patterns, which were collected with scan rates of 0.02° (2θ) per second; the heating rate was 10 °C min^{-1}. The room-temperature XRD patterns were recorded with a Siemens D500 diffractometer, with scan rates of 0.05° (2θ) per second from 5° to 60° (2θ), using Cu Kα radiation ($\lambda = 1.5418$ Å). For the refinement of the lattice parameters, XRD patterns at room temperature were measured in a Philips X′Pert diffractometer, fitted with a Ge(111) incident beam monochromator of the Johansson symmetric type, using Cu $K\alpha_1$ radiation ($\lambda = 1.5405981$ Å) at steps of 0.04° (2θ), from 5° to 60°; the least-squares refinement procedure was carried out with program CELREF.[29]

Table 1. Phases Identified after Mechanical Treatment in Vibrating Mill (VM) and Planetary Mill (PM)[a]

time (h)	VM	PM
1		M
2		M
4		M + A
5	M	M + A
6		A + C
7		A + C
10		A + C
11		A
12		A
18		A
24	M + A	A
48	A + C	A
72	A + C	A
108		A
168	A	

[a] Major components are listed first. M = mixture of initial oxides, A = amorphous, C = $SrCO_3$.

The mechanically activated samples were studied by thermogravimetric analysis (TG) and differential thermal analysis (DTA). The measurements were taken with a Seiko 320 instrument, with α-Al_2O_3 as the inert reference material, between room temperature and 1200 °C in the heating and cooling process in air, at 10° min^{-1}. The evolved gases were analyzed with a Pfeiffer Thermo-Star GSD 301T quadrupole mass spectrometer with argon as gas carrier.

The microstructure was studied with a scanning electron microscope (SEM 960 Zeiss), operated at 10−20 KV, and for the microanalysis an X-ray energy-dispersive spectrometer (EDX Link Isis, Oxford) was used.

Results and Discussion

Synthesis and Characterization. Heat treatment of samples with stoichiometry $SrCO_3/Bi_2O_3/TiO_2$ 1:2:4 at 800 °C for 12 h yields the Aurivillius phase $Bi_4Ti_3O_{12}$ and the perovskite $SrTiO_3$, mixed with a small quantity of strontium bismuth titanate. Cumulative annealing of these phases at 900 °C for 12 more hours yielded $SrBi_4Ti_4O_{15}$ with traces of $Bi_4Ti_3O_{12}$. At the temperature of 1050 °C the strontium bismuth titanate oxide sought is obtained isolated and characterized by XRD as a crystalline material. These evolutions are described in Table 2 under the heading SSR, and we refer to this in what follows as “conventional method”.

Two alternative, mechanochemically assisted routes were tried in the preparation of this compound. In the case of the sample treated in the vibrating mill, the resulting product showed diffractograms where the peaks of the initial products were broadened and progressively less intense. The total grinding time was 168 h, and finally an amorphous state, as judged by XRD, was obtained; this precursor of $SrBi_4Ti_4O_{15}$ (Table 1 and Figure 1), will be hereafter referred to as VM. In the case of the planetary mill, two trials have been made (Figure 2), and in both of them an evolution similar to that of the samples from the vibrating mill was found, i.e., the X-ray diffraction maxima of the reactants became broadened and less intense, and the patterns indicated an amorphous phase. In the first trial the milling was stopped after 12 h, and the XRD difracto-

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Table 2. Phases Identified after Thermal Annealing of Samples Obtained by Solid-State Reaction (SSR), Mechanochemical Activation by Vibrating Mill for 168 Hours (VM), and Mechanochemical Activation by Planetary Mill for 12 h (PM12) and for 108 h (PM108)[a]

treatment (°C/h)	SSR	VM	PM12	PM108
300/1		A + C	A + C^{tr}	A
350/1		F + C	F + C^{tr}	A
400/1		F + C	F + C^{tr}	A + n4^{tr} + n3^{tr}
450/1		F + n4 + C	F + n4 + C^{tr}	n4 + n3
500/1		F + n4 + C	F + n4	n4 + n3
550/1		F + n4	n4 + F	n4
600/1		n4 + F^{tr}	n4	n4
600/5		n4	n4	n4
800/12	S + n3 + n4	n4	n4	n4
900/12	n4 + S + n3^{tr}	n4	n4	n4
1000/12	n4 + S	n4	n4	n4
1050/12	n4	n4	n4	n4
1100/12	n4	n4	n4	n4

[a] Major components are listed first. A = Amorphous, C = $SrCO_3$, S = $SrTiO_3$, F = Sr−Bi−Ti−O−fluorite, n3 = $Bi_4Ti_3O_{12}$, n4 = $SrBi_4Ti_4O_{15}$, ^{tr} = traces. SSR treatments are cumulative; VM, PM12, and PM108 treatments are not cumulative.

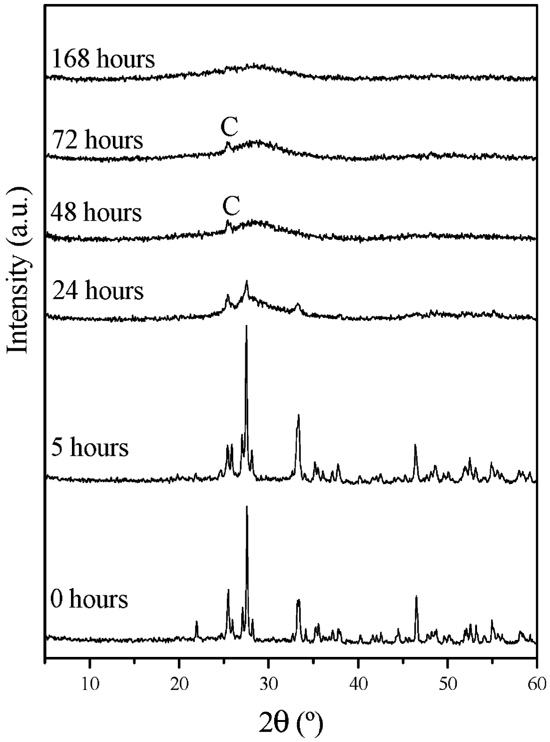

Figure 1. XRD of the reactants (Bi_2O_3, TiO_2, and $SrCO_3$) at different points in the course of mechanical treatment in a vibrating mill (C = $SrCO_3$).

grams corresponded to an amorphous sample precursor (which will be called PM12 in what follows), obtained after milling for a shorter time as compared with one week for the sample from the vibrating mill. In the second trial the initial mixture was activated in the planetary mill during 108 h to attempt mechanosynthesis. The result did not correspond to a crystalline phase, and this amorphous precursor will be referred to in what follows as PM108. In summary, there was no mechanosynthesis in either of the two milling processes.

Thermogravimetry (TG) carried out on sample VM shows three ramps of mass loss (Figure 3a): the first one goes from room temperature to 266 °C and is

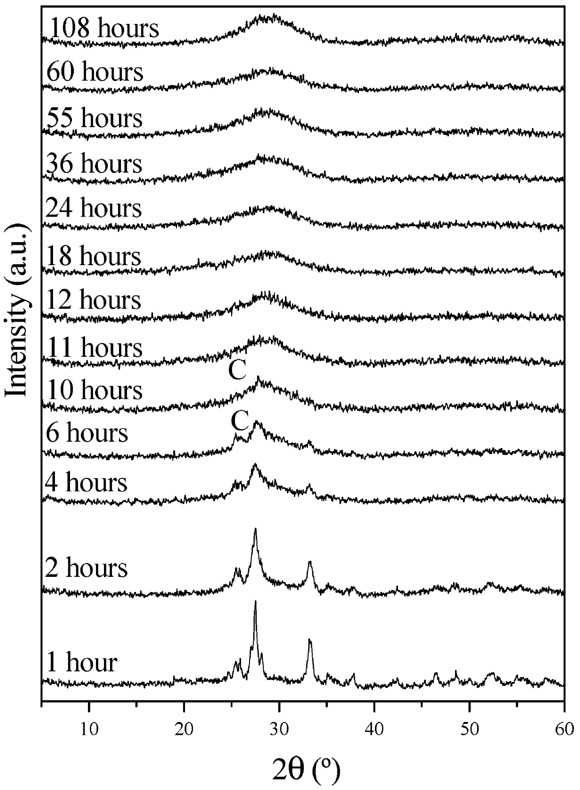

Figure 2. XRD of the reactants (Bi_2O_3, TiO_2, and $SrCO_3$) at several stages of mechanical treatment in a planetary mill (C = $SrCO_3$).

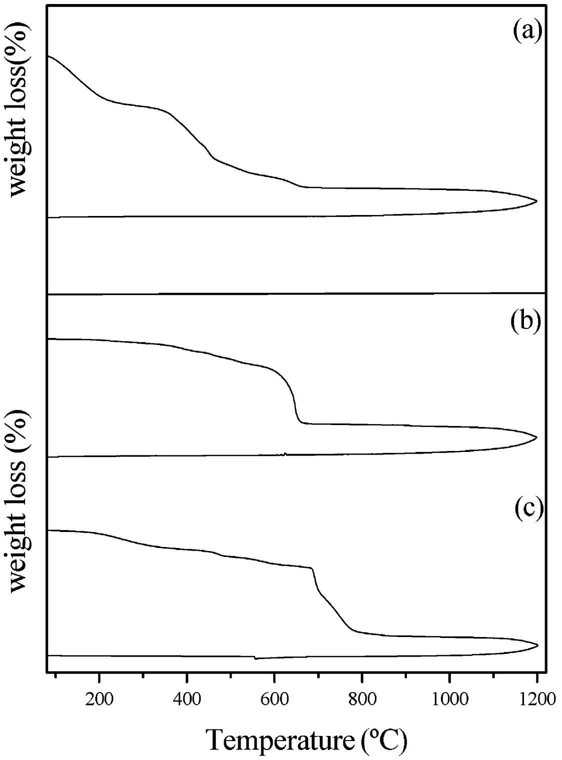

Figure 3. TG curves of samples (a) VM, (b) PM12, and (c) PM108.

attributed (see below) to loss of moisture (2.1% in weight); the second one extends from 266 to 484 °C; and the third one is from 484 to 671 °C. Differential thermal analysis (DTA) exhibits two exothermic peaks on heating, at 376 and 451 °C (Figure 4a); and when cooling,

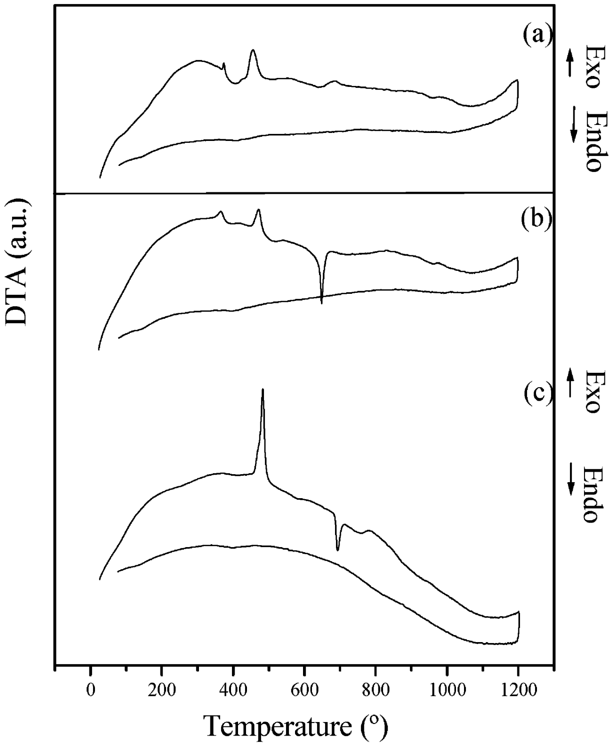

Figure 4. DTA patterns of samples (a) VM, (b) PM12, and (c) PM108.

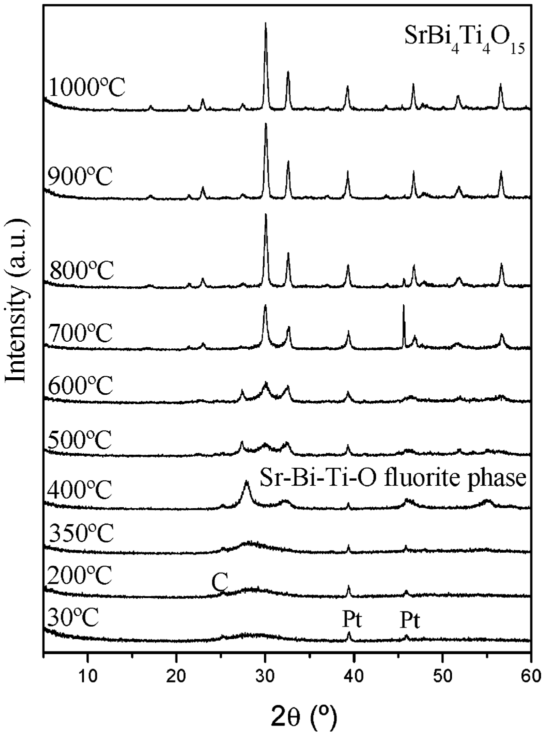

Figure 5. XRD high-temperature patterns of the amorphous precursor VM (C = $SrCO_3$; Pt = platinum).

no peaks are found. The XRD high-temperature patterns (Figure 5) depict the evolution of the powdered precursor with increasing temperature, which helps in the interpretation of the exothermic peaks in DTA and the above-mentioned ramps in the TG graph. The results show that when the precursor is heated to about 200 °C a peak of small intensity appears in the diffractometer pattern close to 25.30° (2θ), corresponding to $SrCO_3$, and this peak does not disappear till 600 °C. This means that the second and the third ramp in the TG data coincide with the loss of CO_2: the second ramp corresponding to that part of CO_2 evolving from the $SrCO_3$ totally activated, and the third one corresponding to the rest of CO_2 coming from that amount of $SrCO_3$ not sufficiently reduced in size by milling (Figure 6). Total CO_2 evolved is about 3.0%, which matches the theoretical value of 3.2%. At 400 °C the XRD trace shows a transitional phase that corresponds with the exothermic peak in the DTA at 376 °C, and the amorphous phase is transformed into a new fluorite-type Sr−Bi−Ti−O phase (Figure 5). Upon increasing the temperature to 500 °C, a change in the sample takes place, coinciding with the second exothermic DTA peak at 451 °C. This can be interpreted as the onset of the formation of the $n = 4$ Aurivillius phase. Both phases, fluorite-type and $SrBi_4Ti_4O_{15}$, coexist at least up to 600 °C, when all CO_2 has been eliminated. Then the fluorite-type phase disappears at 700 °C and the only phase remaining at this temperature and above is pure strontium bismuth titanate oxide, $SrBi_4Ti_4O_{15}$. Further XRD high-temperature work at 1000 °C showed only an increase in crystal perfection in the Aurivillius phase.

The thermal analysis (TG and DTA) of activated sample PM12 (Figures 3b and 4b) is not very different from that obtained on sample VM. Two exothermic peaks are shown, one at 366 °C and the other at 471 °C, together with an endothermic peak at 668 °C; and in the cooling treatment no peak is found. TG data exhibit one ramp from 561 to 693 °C, which coincides with the endothermic peak found in DTA and corresponds to the evolution of CO_2. For sample PM108 (Figures 3c and 4c), the TG data exhibit a single ramp from 684 to 823 °C, and the end temperature is higher than could be expected in view of what happens in the aforementioned sample precursors. DTA from PM108 describes a different thermal behavior in comparison with the evolution of samples VM and PM12. The DTA curve (Figure 4c) presents a unique exothermic peak at 482 °C; and, as it happens in the data from PM12, an endothermic peak appears at about 693 °C. High-temperature XRD on sample PM12 (Figure 7) exhibits an evolution similar to that of the activated precursor VM. At 350 °C the intermediate fluorite-type phase Sr−Bi−Ti−O appears, and coexists mixed with $SrBi_4Ti_4O_{15}$ from 450 to 600 °C; and at 700 °C the Aurivillius compound remains as the single phase. The diffraction peak ($2\theta = 25.40°$) that indicates the presence of $SrCO_3$ appeared at low temperatures when heating the amorphous precursors VM and PM12 (Figures 5 and 7) but in the case of precursor PM108 that peak does not show up in the corresponding XRD diagrams taken at high temperature (Figure 8). Therefore, in the sample PM108 the ramp observed in TG corresponds to the loss of CO_2 (3%) in a single stage, which occurs at a temperature higher than expected. Although the fluorite-type phase Sr−Bi−Ti−O is observed when heating VM and PM12, in the case of sample PM108 that phase cannot be found, and consequently, the synthesis of $SrBi_4Ti_4O_{15}$ does not go through any fluorite intermediate phase. As Figure 8 shows, no transformation occurs in the precursor until the sample reaches 500 °C; at this temperature the Aurivillius phase appears, in agreement with the

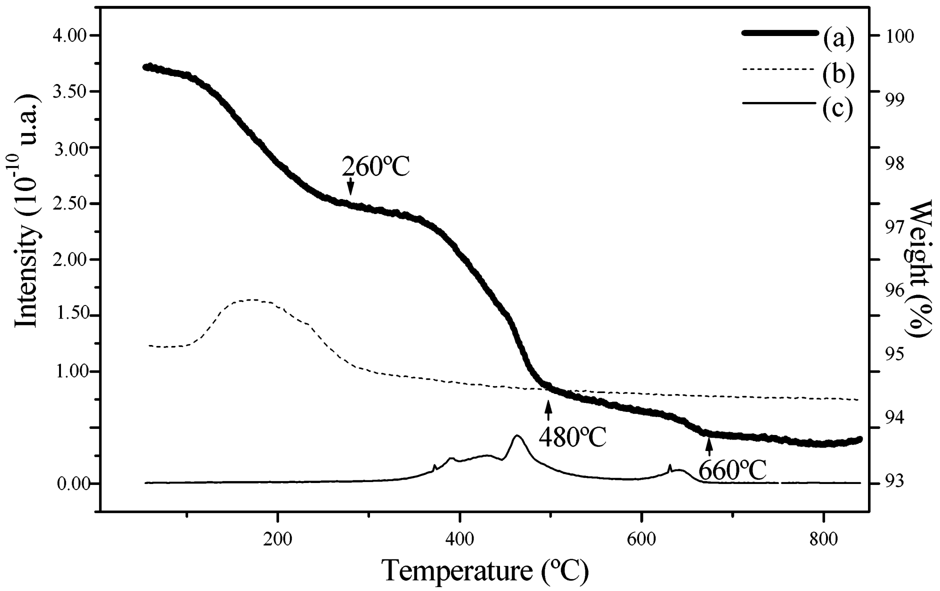

Figure 6. (a) TG-curve of VM; and TG-mass of (b) mass 18 (equivalent to H_2O), (c) mass 44 (equivalent to CO_2).

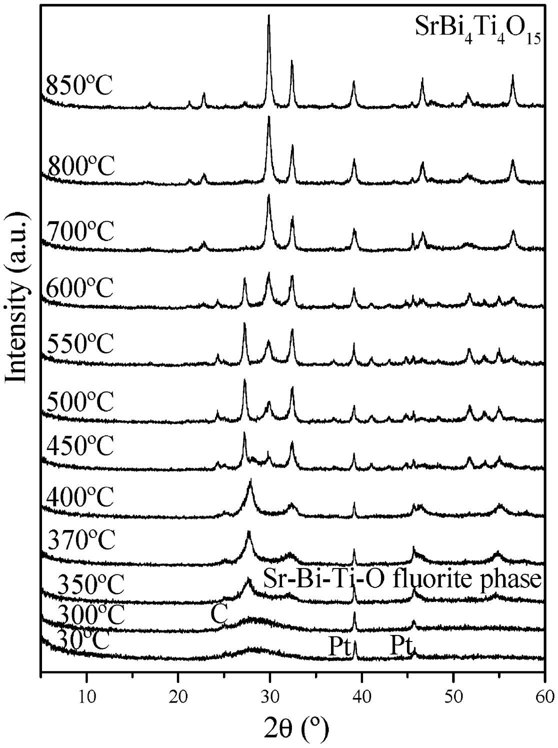

Figure 7. XRD high-temperature patterns of the amorphous precursor PM12 (C = $SrCO_3$; Pt = platinum).

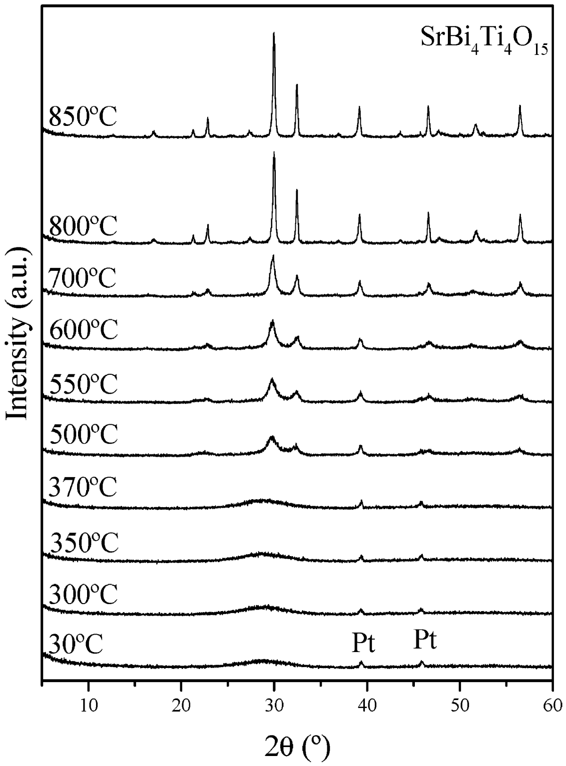

Figure 8. XRD high-temperature patterns of the amorphous precursor PM108 (Pt = platinum).

exothermic peak at 482 °C indicated in DTA. Therefore, that peak corresponds to the transformation from an amorphous to an Aurivillius phase, the crystallinity of which improves steadily with rising temperature.

The subsequent thermal annealing aims at isolating the different phases described by high-temperature XRD (Figures 5, 7, and 8) for samples VM, PM12, and PM108. These treatments are independent, i.e., non cumulative, and the corresponding XRD patterns were taken at room temperature (Table 2). The amorphous sample VM was heated at 350 °C for 1 h and the XRD pattern shows the new fluorite-type Sr–Bi–Ti–O phase, as reported in Table 2. Heating the precursor for 1 h at 450 °C makes $SrBi_4Ti_4O_{15}$ appear together with the fluorite-type phase; heating the precursor at 600 °C during 5 h, we obtain the pure strontium bismuth titanate oxide (Aurivillius phase with $n = 4$), which we expected to synthesize. Therefore, by vibration milling, $SrBi_4Ti_4O_{15}$ is obtained some 400 °C lower than it would be required by a conventional solid-state reaction. From 600 to 1000 °C the crystallinity of this phase improves as each treatment shows. The VM precursor heated in a cumulative treatment from 1 h plus 4 h plus 7 h at 1000 °C (Figure 9) changes into an ordered, crystalline structure. The lattice parameters were refined for $SrBi_4Ti_4O_{15}$ using our measured 2θ data and the Miller indices in JCPDS card no. 43-0973. The final values of the refined

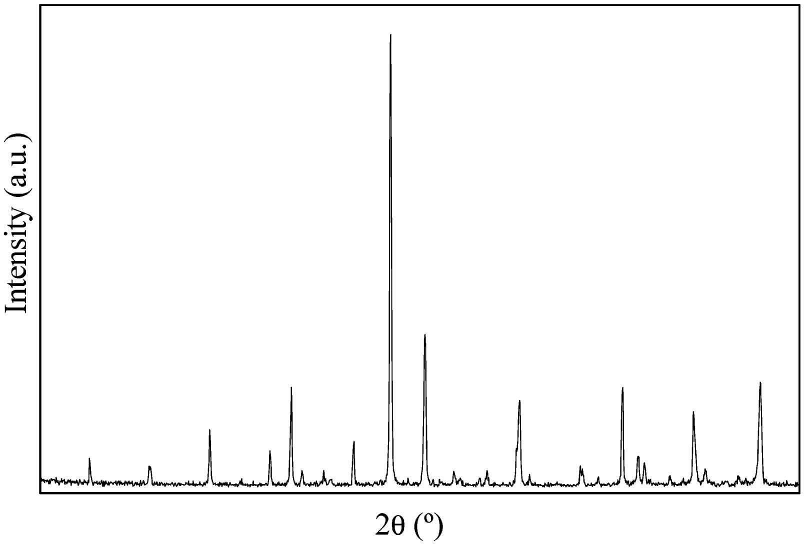

Figure 9. XRD at room temperature of $SrBi_4Ti_4O_{15}$ heated at 1000 °C for 1 + 4 + 7 h.

cell parameters at 25 °C, $a = 5.4510(7)$ Å, $b = 5.4399(7)$ Å, and $c = 40.994(5)$ Å, for this orthorhombic material are in good agreement within experimental error with the values in Hervoches et al.[17] and they do not deviate much from those in Nalini et al.[30]

The ground precursor PM12 showed in the noncumulative treatments (Table 2) a behavior similar to that of the activated sample VM, as evidenced by XRD data at room temperature; the fluorite type Sr−Bi−Ti−O and $SrBi_4Ti_4O_{15}$ phases are obtained together at 450 °C, and after heating at 600 °C for 1 h the Aurivillius compound remains as the single phase. The amorphous sample PM108, when heated at 450 °C, transforms into Aurivillius phases ($n = 3$ and 4, not well defined), without a hint of the fluorite phase. If sample PM108 is subjected to 550 °C for 1 h, the Aurivillius phase $SrBi_4Ti_4O_{15}$ is isolated. The evolution from this temperature upward is similar to that of the other samples, with improvement in the crystallite quality.

The results in this discussion show that pure $SrBi_4Ti_4O_{15}$ can be obtained by the traditional route after several cumulative heating periods of 12 h each, at the final temperature of 1050 °C; in contrast, the precursor samples VM and PM12 obtained by mechanical activation, produce the oxide mixed with the fluorite phase after 1 h at 450 °C, and the pure phase when the precursors are heated at 600 °C for 5 and 1 hours, respectively. In the case of the precursor PM108, the pure Aurivillius phase is obtained after 1 h at 550 °C. Longer heating times and higher temperatures can therefore be dispensed with when starting with a precursor which has previously been mechanically activated.

Morphological Study. The evolution from the precursors to the final Aurivillius oxide can also be followed by the changes in the morphology of the grains, as evidenced by SEM photographs. A micrograph of the initial mixture Bi_2O_3, TiO_2 (anatase), and $SrCO_3$ used for both the ceramic method and the milling processes is shown in Figure 10a. Three different kinds of particles with sizes ranging from 1.5 to 20 μm are present in the picture, but only Bi_2O_3 can be clearly distinguished by its large laminar particles. When the reagents are heated to a temperature of 1100 °C, after cumulative successive treatments (Table 2), the sample (see Figure 10b) is a single phase with laminar aspect typical of the Aurivillius family.

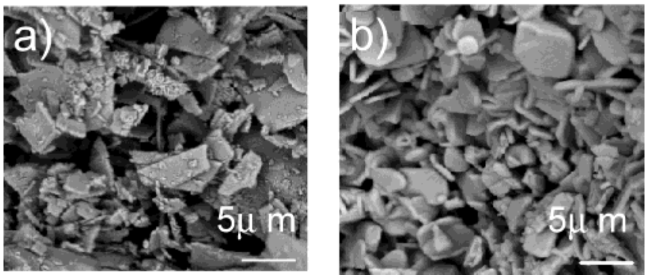

Figure 10. Scanning electron micrographs of (a) initial reactants (Bi_2O_3, TiO_2, and $SrCO_3$) and (b) mixture of oxides heated to 1100 °C after 12 h of cumulative treatments.

The activated precursor VM shows a homogeneous fine-grained morphology (Figure 11a) which significantly departs from the morphology of the initial products (Figure 10a). The size of the spherical grain (300 nm) is much smaller than that of the initial products (10 μm on the average). The micrograph of the sample heated at 400 °C exhibits a crystalline tabular phase and spherical aggregates of smaller particles (Figure 11b). The crystal tablets have a triangular shape suggesting cubic symmetry, as the photo shows in some parts, and in view of the results of XRD, this phase is identified as the fluorite Sr−Bi−Ti−O. The spherical particles are 280 nm in diameter and apparently preserve the amorphous structure of the precursor. After heating the precursor at 550 °C for 1 h, the sample presents agglomerates and spherical particles (Figure 11c). These spherical grains, about 330 nm in diameter, show a slight increase in grain size in comparison with those in the sample at 400 °C. XRD reveals that the new fluorite-type still exists at this temperature, although it cannot be made out in the micrograph; and in the same way, the Aurivillius phase cannot be clearly identified. After 5 h at 600 °C, the XRD pattern indicates that strontium bismuth titanate oxide is isolated, but the aspect of the powder, as revealed by SEM, shows little difference with respect to that of the sample treated at 550 °C: only spherical particles (370 nm in

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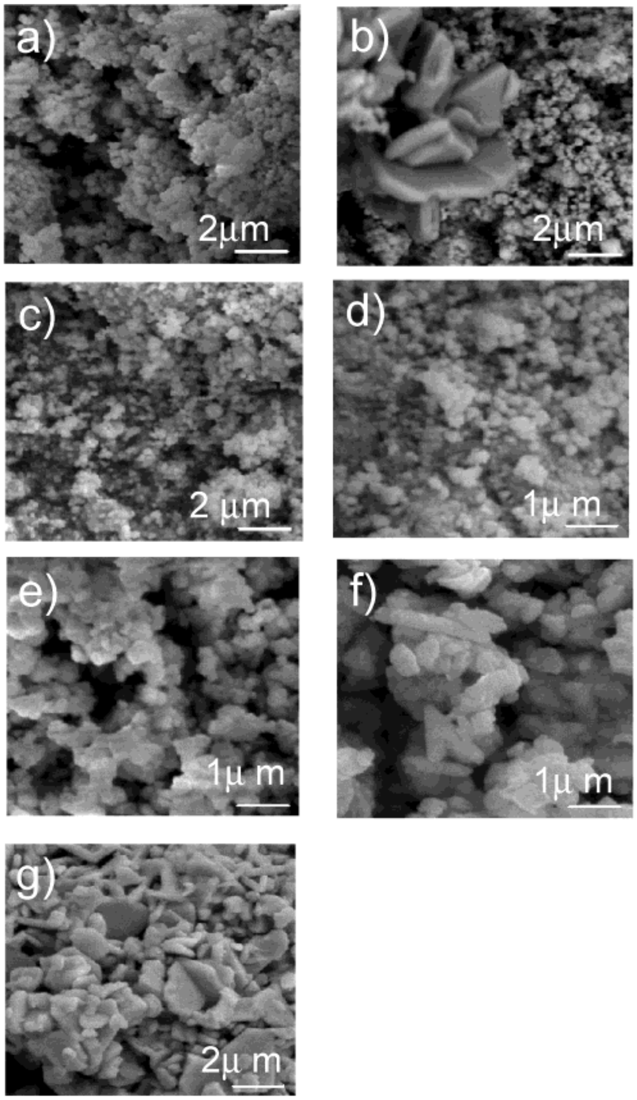

Figure 11. Scanning electron micrographs of (a) VM; (b) precursor VM heated at 400 °C (1 h); (c) precursor VM heated at 550 °C (1 h); (d) precursor VM heated at 600 °C (5 h); (e) precursor VM heated at 800 °C (1 + 4 + 7 h); (f) precursor VM heated at 900 °C (1 + 4 + 7 h); and (g) precursor VM heated at 1000 °C (1 + 4 + 7 h).

diameter) and agglomerates are observed (Figure 11d), perhaps a little larger. The shape and size of the particles after treatment at 800 °C (cumulative treatment of 1 plus 4 plus 7 h) indicate an increase in crystal perfection, although a few particles still show spherical shape (Figure 11e), with an average size of about 512 nm. In Figure 11f, a micrograph of the sample after treatment at 900 °C (1 plus 4 plus 7 h), a change in the grain shape can be seen. The laminar morphology characteristic of the Aurivillius phase is now plentiful, and the smaller particles do not look like spheres anymore. The tablet thickness is around 220 nm, and the largest dimension ranges from 260 to 1680 nm; then, the size increased in relation to that of the particles in Figure 11e. After treatment at 1000 °C (1 plus 4 plus 7 h), most grains acquire the tabular morphology typical of Aurivillius phases, and hence we are in the presence of a well-crystallized single-phase material (Figure 11g), growing in platelets with a thickness of 650 nm and ranging from 939 to 2993 nm approximately in the other dimensions.

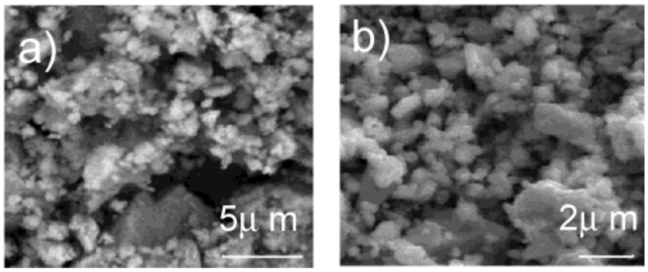

Figure 12. Scanning electron micrographs of samples (a) PM12 and (b) PM108.

The morphology of the amorphous PM12 (Figure 12a) consists of spherical particles and agglomerates. On the other hand, the activated sample PM108 (Figure 12b) is composed by spherical grains with no agglomerates. In both cases there are spherical grains, similar in size, with an average diameter of 450 nm. Elemental analysis (EDX) carried out on several particles reveals that the composition is about 45−46% of Bi^{III}, 45−46% of Ti^{IV}, and 8.7−9.5% of Sr^{II}. The metal atom ratios are Bi/Ti/Sr = 4:4:1, which amounts to 44% of Bi^{III}, 44% of Ti^{IV}, and 11% of Sr^{II}, the theoretical stoichiometry for $SrBi_4Ti_4O_{15}$.

The morphology of the different precursors heated at various temperatures shows the homogeneity of the mechanically activated precursors, in contrast with the heterogeneity of the initial reagents; and the nanometer size of the particles so activated makes possible a reduction in the temperature and heating time required for the synthesis of the material.

Conclusions

We show in this article that the formation of $SrBi_4Ti_4O_{15}$, an Aurivillius phase with $n = 4$, can be accomplished after heating the amorphous precursors VM, PM12, and PM108 for 1 h at a temperature as low as 450 °C.

The material can be obtained as a single phase in two ways: (1) milling the reactants for 168 h in a vibrating mill (sample VM) or 12 h in a planetary mill (sample PM12), followed by thermal treatment at 600 °C for 5 h (VM) and 1 h (PM12); (2) milling the reactants for 108 h in a planetary mill (sample PM108) followed by heating at 550 °C for 1 h.

Both procedures represent considerable gain over the ceramic solid-state reaction, which requires several heating treatments and grindings and is complete only after heating at 1050 °C.

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