Mechanochemical activation assisted synthesis of bismuth layered-perovskite SrBi$_4$Ti$_4$O$_{15}$

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Strontium bismuth titanate oxide (SrBi$_4$Ti$_4$O$_{15}$) belongs to the Aurivillius structural type. The materials in this family are good candidates as lead-free ferroelectric materials for applications at high temperature due to their elevated Curie temperature. The mechanochemical activation method permits one to reduce the particle size of the initial products, so the specific surface is increased, improving in most cases its reactivity. In this paper we report on the synthesis of SrBi$_4$Ti$_4$O$_{15}$ Aurivillius-type material from activated precursors, obtained though mechanical treatment in vibrating and planetary mills. In some samples a new transitory Sr-Bi-Ti-O fluorite-type phase appears, depending on the milling time and the kind of mill used. The synthesis of SrBi$_4$Ti$_4$O$_{15}$ from activated precursors is obtained at a temperature about 450°C lower than it would have been required by a conventional solid-state reaction, with significantly reduced heating times.
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1. Introduction

Lead-free Aurivillius phases [1] have been investigated in the last decade for their ferroelectric behaviour at high temperatures [2, 3] (Curie temperature in the range of 500°C and upwards [4]) with important applications as ferroelectric materials [5].

The framework of the Aurivillius family consists of layers of Bi$_2$O$_2$ where Bi^{3+} can be partially substituted for by cations having a lone pair of electrons [6], intercalated with peroskite-type layers of the form A$_{n-1}$B$_n$O$_{3n+1}$, where n is the number of perovskite-like stacked layers [7], and where the voluminous cation is A [8–11], and B makes up the octahedra (BO$_6$) [12, 13], linking with Bi$_2$O$_2$ blocks.

The mechanochemical activation method [14, 15] has been proposed as an alternative to avoid the problems presented by the solid-state method. The particle size is controlled during the mechanical treatment and losses in stoichiometry are less probable, given the decrease in the time and temperature of heating [16]; moreover the ferroelectric properties of the ceramic improve by this method [17–19].

SrBi$_4$Ti$_4$O$_{15}$ [13, 20] has been synthesized in this work by the mechanoactivation route from Bi$_2$O$_3$, TiO$_2$ (anatase) and SrO as initial reagents. The mechanical treatments have been carried out using vibrating and planetary mills.

2. Experimental

The ceramic and mechanochemical activation methods of synthesis have been carried out on stoichiometric amounts of the reactants to yield 3 grams of SrBi$_4$Ti$_4$O$_{15}$, the powder being initially homogenized by hand in an agate mortar. For solid-state reaction (SSR) the Bi$_2$O$_3$ (Cerac, 99.9% pure), TiO$_2$ (anatase, Cerac, 99.5% pure) and SrCO$_3$(Cerac, 99.9% pure) were the initial products used. The cumulative sequence heating was 12 h at 800, 900, 1000 and 1050°C, respectively. After each heat treatment, a homogenization by hand and a characterization by X-ray powder diffraction (XRD) at room temperature were carried out.

In the mechanochemical activation procedure three precursors were obtained from the vibrating and planetary mills, using as initial products Bi$_2$O$_3$, TiO$_2$ (anatase) SrO (Aldrich 99.9% pure, weighed in argon atmospher because of its high reactivity with atmosphere water and CO$_2$). The mills are composed by a stainless steel vessel and balls, one 5 cm diameter in the vibrating mill and five 1 cm diameter in the planetary mill (Fritsch, Pulverizette models 0 and 6, respectively). The activated samples were characterized by X-ray diffraction at different temperatures, as reported elsewhere [21].

Thermogravimetric (TG) and differential thermal analyses (DTA) were carried out on the mechanically treated precursors; the curves (between room temperature and 1200°C in the heating and cooling process in air, at 10 K/min) were taken using a Seiko 320 instrument, with α-Al$_2$O$_3$ as the inert reference material.

The morphological study was accomplished with a scanning electron microscope (SEM 960 Zeiss), operated at 10–20 kV.

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3. Results and discussion

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, yields $SrBi_4Ti_4O_{15}$. At the temperature of $1050°C$ the strontium bismuth titanate oxide is obtained isolated, and characterized by XRD as a crystalline material. These evolutions are reported in Table I, under the heading SSR.

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 sample shows diffraction patterns where the peaks of the initial products are broadened and progressively less intense; however, when milling time reaches 72 h, a small but quite sharp peak of $SrCO_3$ appears indicating carbonation of SrO during mechanical activation (Table II). After 168 hours of milling, the mechanical treatment is considered complete (Fig. 1a). This precursor of $SrBi_4Ti_4O_{15}$ shall hereafter referred to as VS. In the case of the planetary mill, two trials were made, and in both of them the X-ray diffraction maxima became broadened and less intense. In the first case, the milling was stopped after 12 h and the XRD patterns (sample PS12) corresponded to an amorphous sample precursor with a tiny peak indicating the presence of $SrCO_3$ (Table II), as in VS, but weaker in intensity. In the second case, the initial mixture was activated in the planetary mill during 90 h, to attempt mechanosynthesis [22]. The resulting precursor was totally amorphous (Table II), and will be referred to as PS90.

TABLE I Phases identified after thermal treatment of the sample obtained by solid-state reaction in cumulative treatments (SSR), and by mechanochemical activation by vibrating mill (VS168) and mechanochemical activation by planetary mill (PS12, PS90) in non-cumulative treatments

Thermal treatment (°C/hours)	SSR	VS	PS12	PS90
300/1	–	A + C	A + C	A
350/1	–	F + C^{tr}	F + C^{tr}	A
400/1	–	F + C^{tr}	F + n4	A + n4 + $n3^{vlc}$
450/1	–	F + n4 + C^{tr}	F + n4	n4 + n3 + A^{tr}
500/1	–	n4 + F + C^{tr}	F + n4	n4 + n3 + A^{tr}
550/1	–	n4 + F + C^{tr}	F + n4	n4 + n3 + A^{tr}
600/1	–	n4 + F + C^{tr}	n4	n4
600/1 + 4	–	n4	–	–
700/1	–	n4	–	–
800/1	–	n4	n4	n4
800/12	S + n3 + n4	–	–	–
900/1	–	n4	n4	n4
900/12	n4 + S + n3	–	–	–
1000/1	–	n4	n4	n4
1000/12	n4 + S	n4	–	–
1050/1	–	n4	–	n4
1050/12	n4	–	–	–
1100/12	n4	–	–	–

A = Amorphous, C = $SrCO_3$, S = $SrTiO_3$, F = Sr-Bi-Ti-O fluorite phase, n3 = $Bi_4Ti_3O_{12}$, n4 = $SrBi_4Ti_4O_{15}$, tr = traces, vlc = very low cristallinity. Major components are listed first.

TABLE II Phases identified after mechanical treatment in vibrating mill and planetary mill

Time of milling (hours)	Vibrating mill	Planetary mill
1	–	–
2	–	M
4	–	M
5	M	M + A
6	–	–
7	–	A + M
12	–	A + C^{tr}
18	–	A
24	M + A	A
36	–	A
48	–	A
60	–	A
72	C + A	A
90	–	A
108	–	–
144	A + C	–
168	A + C	–

M = mixture of initial oxides, A = Amorphous, C = SrCO3, tr = traces. Major components are listed first.

Sample VS gives two main TG ramps of mass loss; the first one goes from room temperature to approximately $400°C$, and is attributed to the loss of moisture (3.9% in weight); and the second one (around $440°C$) corresponds to 0.38% in weight. Differential thermal analysis (DTA) exhibits two exothermic peaks on heating, at $382°C$ and $451°C$. The high-temperature XRD patterns depict the evolution of the powdered
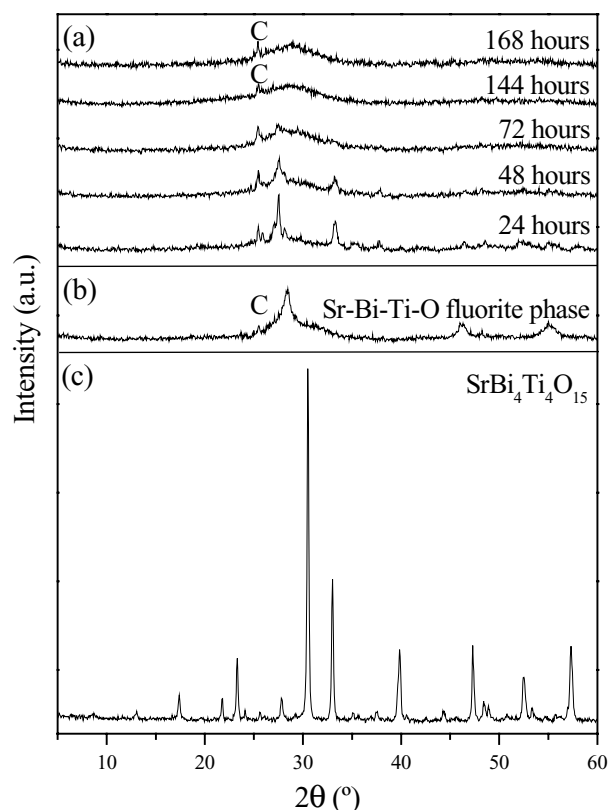

Figure 1 (a) XRD pattern of initial reactants (Bi_2O_3, TiO_2 and SrO) during mechanical treatment in a vibrating mill (C = $SrCO_3$); (b) transitional phase, precursor VS heated at $350°C$ for 1 h; (c) Aurivillius phase, precursor VS heated at $1000°C$ for 12 h.

precursor with increasing temperature. A small intensity of $SrCO_3$ peak appear at 200°C in the pattern, and it is visible up to 600°C. Therefore, the second ramp in the TG data coincide with the loss of CO_2 from SrO carbonated during the milling procedure. At the temperature of 400°C the XRD trace shows a transitional phase that corresponds with the exothermic peak in the DTA at 382°C, and is interpreted as a fluorite-type Sr-Bi-Ti-O phase. 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; the fluorite-type phase is no longer visible at 700°C, and the only phase remaining at this temperature and above is the strontium bismuth titanate oxide alone, i.e., $SrBi_4Ti_4O_{15}$. Further increase of the temperature (up to 1000°C) is accompanied only by an increase in crystal perfection in the Aurivillius phase.

TG and DTA results of activated sample PS12 are not very different from those obtained on sample VS. Two exothermic DTA peaks are shown, one at 368°C, and other at 434°C. TG data exhibit two gentle ramps from room temperature to 374°C (corresponding up to water evolution) and from 400 to 460°C (0.09% loss in weight) which can be attributed to the evolution of CO_2. For sample PS90, the TG data exhibit a single ramp at around 380°C. DTA from PS90 describes a different thermal behavior in comparison with the evolution of the samples VS and PS12. The DTA curve presents a unique exothermic peak at 454°C. High-temperature XRD on the sample PS12 exhibits an evolution similar to that of the activated precursor VS. At 350°C the intermediate fluorite-type phase Sr-Bi-Ti-O appears, and coexists mixed with $SrBi_4Ti_4O_{15}$ from 400 to 600°C; and at 700°C the Aurivillius phase remains alone. The diffraction peak (at $2\theta = 25.40°$) that indicates the presence of $SrCO_3$ appeared at low temperatures when heating the amorphous precursors VS and PS12. In the case of the precursor PS90, that peak does not show up in the corresponding XRD diagrams taken at high temperature. Although the fluorite-type phase Sr-Bi-Ti-O was observed when heating the samples VS and PS12, in the case of sample PS90 that phase could not be found. No transformation occurred in the precursor until the sample reached 450°C; at this temperature the Aurivillius phase appears, in agreement with the exothermic peak at 454°C shown in DTA curve. Therefore, that peak corresponds to the transformation from an amorphous to an Aurivillius phase, whose crystallinity improves with rising temperature.

The subsequent thermal annealing aims at isolating the different phases found in the high-temperature XRD patterns for samples VS, PS12 and PS90. These treatments are independent, i.e., not cumulative, and the XRD patterns were taken at room temperature (Table I). Sample VS was heated at 350°C for one hour and the XRD shows the fluorite-type Sr-Bi-Ti-O phase, as the data on Table I and Fig. 1b show. Heating the precur-

sor for one hour at 450°C leads to the formation of $SrBi_4Ti_4O_{15}$ accompanied by 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 wanted to synthesize. Therefore by vibration milling, $SrBi_4Ti_4O_{15}$ is obtained at temperatures that are about 450°C lower than those at which this material would be prepared by the solid-state reaction. In the temperature range from 600 to 1000°C, the crystallinity of this phase improves (see Fig. 1c).

Precursor PS12 exhibited in the non-cumulative treatments (Table I) a behavior similar to that of sample VS, as evidenced by XRD at room temperature; the fluorite type Sr-Bi-Ti-O and $SrBi_4Ti_4O_{15}$ phases are obtained together at 400°C, and after heating at 600°C for 1 h, the Aurivillius phase is isolated. The amorphous sample PS90 transforms when heated at 400°C, into Aurivillius phases, without traces of the fluorite-type phase. If sample PS90 is subjected to 600°C for 1 h, the Aurivillius phase $SrBi_4Ti_4O_{15}$ is isolated. The evolution from this temperature upwards is similar to that of the other samples, with improvement in the crystallite quality.

This discussion shows that pure $SrBi_4Ti_4O_{15}$ can be obtained by the traditional procedure after several cumulative heating periods of 12 h each, at the final temperature of 1050°C; in contrast, the precursor samples VS and PS12, obtained by mechanical activation, produce the oxide mixed with the fluorite-phase after 1 h at 450°C, and the pure phase when they are heated at 600°C for 5 and 1 h, respectively. In the case of the precursor PS90, the pure Aurivillius phase is obtained after 1 h at 600°C. Long heating times and high temperatures can be substantially reduced if the precursor has previously been mechanically activated.

The evolution from the precursors to the mixed oxide can also be followed by the changes in the morphology of the grains, as evidenced by SEM photographs. The activated precursor VS shows (Fig. 2a) round and huge particles (with a size of about 1200 nm in average) that could be $SrCO_3$; around these particles and in agglomerates there are spherical grains with a grain size of 210 nm. The micrograph of the sample heated at 350°C exhibits agglomerates and spherical particles of 140 nm in diameter (Fig. 2c). The $SrCO_3$ and the Sr-Bi-Ti-O fluorite phase identified by XRD with low crystallinity, are not distinguished in this micrograph. After 5 h at 600°C, the sample presents agglomerates and spherical particles with the size of about 180 nm (Fig. 2d), and apparently conserves the structure of the sample treated at 350°C, although the XRD pattern indicates that strontium bismuth titanate oxide is isolated. Then, it can be conclude that the Aurivillius phase existing at this temperature, exhibits crystals having a spherical shape, with very small size. The shape and size of the particles after treatment at 800°C (1 h) indicate an increase in crystal perfection, the morphology is irregular and not totally defined (Fig. 2e). After treatment at 1000°C (1 h) a unique phase is exhibited, and most of the grains present a tabular morphology characteristic
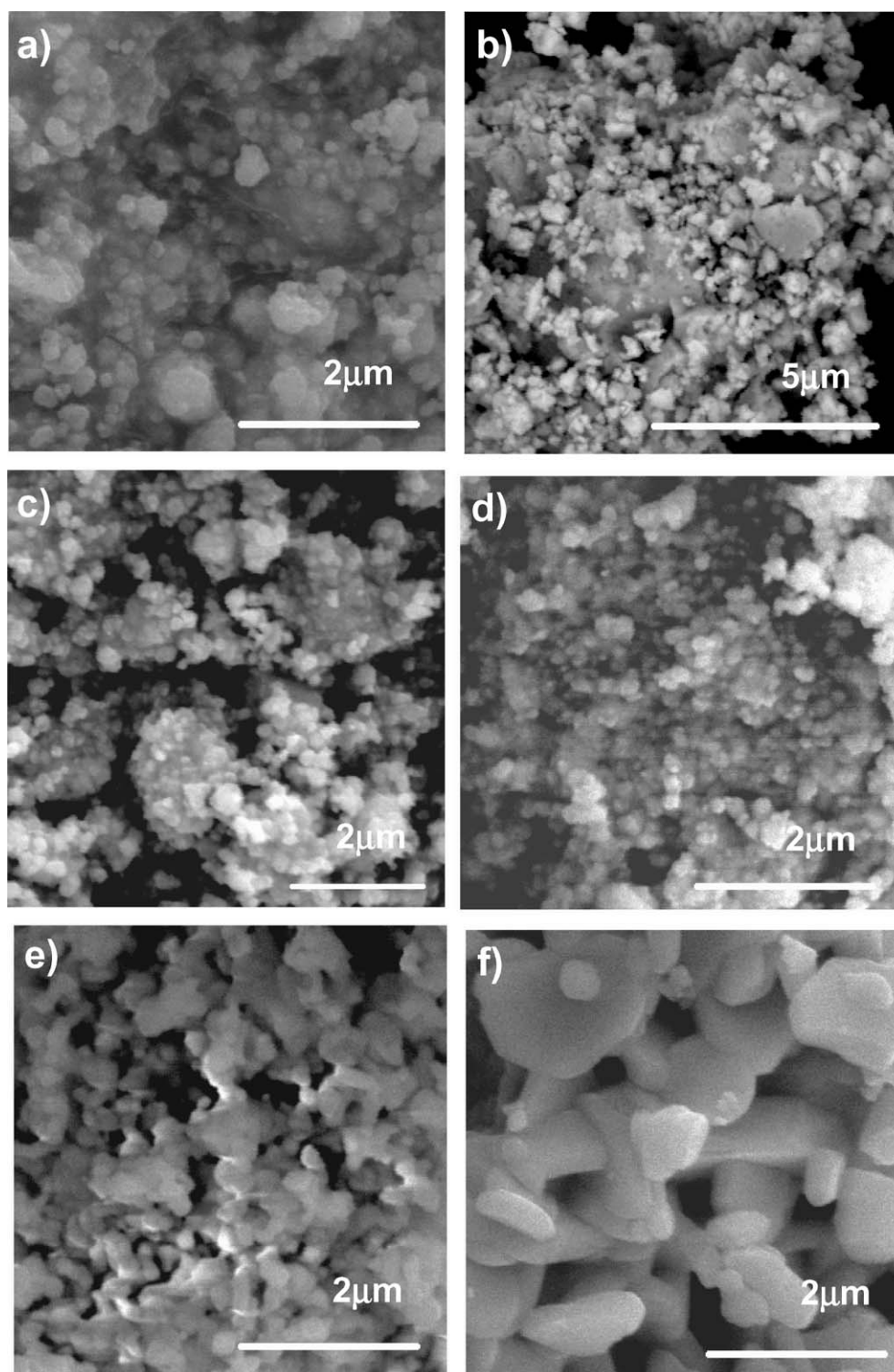
Figure 2 Scanning electron micrographs of (a) precursor VS; (b) precursor PS90; (c) precursor VS heated at 350°C (1 h); (d) precursor VS heated at 600°C (1 + 4 h); (e) precursor VS heated at 800°C (1 h); (f) precursor VS heated at 1000°C (1 h).

of Aurivillius phases (Fig. 2f). Then, a well crystallized single phase material is grown, the platelets ranging from 1200 to 2800 nm, with a thickness of about 410 nm.

The morphology of precursor PS90 (Fig. 2b) consists of rounded particles as in sample VS, and small grains exhibiting an irregular aspect, 110 to 540 nm in size. So, from the viewpoint of the morphology, the precursors VS and PS are nearly equivalent.

In summary the nanometer size of the mechanically activated precursor particles, observed by SEM, favors the diminution of temperature and time of annealing necessary to obtain the Aurivillius phase; thus, making the synthesis of the material easier.

4. Conclusions

The synthesis of $SrBi_4Ti_4O_{15}$ by a mechanochemical route has been carried out through three different ways: the first treatment consists of milling the reactants for 168 h in a vibrating mill (VS) and the phase is synthesized by heating for 5 h at 600°C; the second and the third routes consist of milling the reactants for 12 and 90 h, respectively, in a planetary mill, and

both yield the required phase after heating for 1 h at 600°C.

We have obtained the oxide in one step at temperatures that are about 450°C lower than those characteristic for the conventional SSR, and reducing the heating time to 1 or 5 h. Thus, mechanochemical activation is seen to improve the synthesis of the bismuth layered oxide.

Acknowledgment

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