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Optimization of the mechanochemical conditions for the synthesis of the xBiFeO$_3$–(1 − x)PbTiO$_3$ multiferroic system

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ABSTRACT

The xBiFeO$_3$–(1 − x)PbTiO$_3$ solid solution is nowadays one of the most promising multiferroic systems. However, the obtaining of single phases with a high crystallinity is difficult by the conventional methods. In this work, the mechanochemical method has been optimized, testing different parameters in the reaction to obtain the suitable conditions of synthesis. The investigated parameters were: the atmosphere conditions and the material of the reaction medium. Single phases with compositions belonging to the whole system ($0 \leq x \leq 1$) have been obtained, being the mechanochemical reaction with tungsten carbide vessel the best synthesis medium. The structural characterization of the obtained powders has been carried out by XRD and microstructures of powdered samples have been studied by SEM and TEM.

1. Introduction

Nowadays, one of the most promising multiferroic materials is the BiFeO$_3$, an oxide with high Curie (825 °C) and Néel (370 °C) temperatures [1]. This compound is ferroelectric and antiferromagnetic at room temperature, and it is a good candidate to study the magnetoelectric effect, interesting property from the point of view of its numerous applications [2]. The most common problems of this rhombohedral perovskite (space group $R3c$, No. 161) are related to its high conductivity and antiferromagnetic character, which does not allow a net magnetization [1,3].

In order to improve the ferroelectric and the magnetic properties, many cationic substitutions have been carried out in the perovskite structure [4], being one of the most promising possibilities the solid solution xBiFeO$_3$–(1 − x)PbTiO$_3$ (BF–PT) [5]. The PbTiO$_3$ is a tetragonal perovskite (S.G. $P4mm$, No. 99) with a T_C = 490 °C and very good ferroelectric properties [6]. The substitution of Pb^{2+} for Bi^{3+} improves the ferroelectric properties [7,8], while the substitution of Ti^{4+} for Fe^{3+} increases the stability of the perovskite structure and the magnetic properties, since the modulated antiferromagnetic spiral structure is destroyed and a weakly ferromagnetic state appears [3]. This solid solution exhibits a morphotropic phase boundary (MPB) between the rhombohedral symmetry (BiFeO$_3$-rich region) and the tetragonal one (PbTiO$_3$-rich region) both with perovskite structure, although there is still some controversy about the localization and the width of this range of coexistence of both polymorphs [9].

In the bibliography, the synthesis of the xBiFeO$_3$–(1 − x)PbTiO$_3$ system has been reported in many works, but in most of them the apparition of secondary phases (Bi$_2$Fe$_4$O$_9$ and Bi$_{24}$FeO$_{39}$) in the synthesis process of the BF-rich compositions is reported [10]. Several synthesis routes have been employed to obtain different compositions of this system, some examples are: solid-state route [11], co-precipitation [12], sol–gel combustion [13] or microwave-hydrothermal synthesis [14]. In most of them low temperature is used in the synthesis, because of the BiFeO$_3$ decomposition at 830 °C or higher temperatures [15].

In this sense, mechanochemical methods help the formation of perovskite-type oxides at low temperature, due to the increase of the reactivity, during the milling process, both by mechanoactivation of reactants and further annealing at moderate temperatures [16,17] or by direct mechanosynthesis at room temperature [18–21], even allowing high-pressure metastable phases to be isolated without the application of external pressure [22]. Other authors have previously used the high-energy milling as synthesis method only for one composition in the MPB region (0.7BiFeO$_3$–0.3PbTiO$_3$) of the present solid solution. Different results were obtained depending on the mechanochemical conditions, Khan et al. [23] obtained mechanically activated powders, which transform to the single phase of 0.7BiFeO$_3$–0.3PbTiO$_3$ after low-temperature calcinations, while Zhang et al. [24] obtained this mechanosynthesized powder, employing a different milling system.

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Table 1
Identified phases and experimental conditions of the different methods of synthesis of $x\mathrm{BiFeO_3}$–$(1-x)\mathrm{PbTiO_3}$ system (xBF–$(1-x)$PT).

Composition	Milling time (h)	Identified phases after milling process	Annealing temperature (°C) (annealing time (h))	Identified phases after thermal treatments
Ceramic route				
PT			700 (12)	$PbTiO_3$ (T)
0.3BF–0.7PT			1000 (12)	0.3BF–0.7PT (T)
0.5BF–0.5PT			1050 (12)	0.5BF–0.5PT (R and T)
0.6BF–0.4PT			950 (12)	0.6BF–0.4PT (R and T)
0.7BF–0.3PT			900 (12)	0.7BF–0.3PT (R and T)
0.9BF–0.1PT			900 (12)	0.9BF–0.1PT (R), $Bi_2Fe_4O_9$
BF			800 (12)	$BiFeO_3$ (R), $Bi_2Fe_4O_9$, $Bi_{25}FeO_{40}$
Mechanoactivation steel/air				
0.3BF–0.7PT	140	0.3BF–0.7PT (LC), Bi	800 (12)	0.3BF–0.7PT (T)
0.5BF–0.5PT	140	0.5BF–0.5PT (LC), Bi	800 (12)	0.5BF–0.5PT (T)
0.7BF–0.3PT	140	Amorphous phase	800 (12)	$Bi_2Ti_2O_7$, reactants
BF	140	Amorphous phase	800 (12)	$BiFeO_3$ (R), $Bi_2Fe_4O_9$, $Bi_{25}FeO_{40}$
Mechanoactivation steel/O_2				
0.3BF–0.7PT	70	0.3BF–0.7PT (LC)	800 (12)	0.3BF–0.7PT (T)
0.5BF–0.5PT	70	0.5BF–0.5PT (LC)	800 (12)	0.5BF–0.5PT (T)
0.7BF–0.3PT	140	Amorphous phase	800 (12)	0.7BF–0.3PT (R and T)
BF	140	Amorphous phase	800 (12)	$BiFeO_3$ (R), reactants
Mechanoactivation WC/air				
PT	24	PT (LC)	1050 (2)	$PbTiO_3$ (T)
0.1BF–0.9PT	24	0.1BF–0.9PT (LC)	1050 (2)	0.1BF–0.9PT (T)
0.2BF–0.8PT	24	0.2BF–0.8PT (LC)	1050 (2)	0.2BF–0.8PT (T)
0.3BF–0.7PT	24	0.3BF–0.7PT (LC)	1050 (2)	0.3BF–0.7PT (T)
0.4BF–0.6PT	24	0.4BF–0.6PT (LC)	1050 (2)	0.4BF–0.6PT (T)
0.5BF–0.5PT	24	0.5BF–0.5PT (LC)	1050 (2)	0.5BF–0.5PT (T)
0.6BF–0.4PT	24	0.6BF–0.4PT (LC)	1050 (2)	0.6BF–0.4PT (T)
0.625BF–0.375PT	24	0.625BF–0.375PT (LC)	1050 (2)	0.625BF–0.375PT (R and T)
0.65BF–0.35PT	24	0.65BF–0.35PT (LC)	1050 (2)	0.65BF–0.35PT (R and T)
0.675BF–0.325PT	24	0.675BF–0.325PT (LC)	1050 (2)	0.675BF–0.325PT (R and T)
0.7BF–0.3PT	24	0.7BF–0.3PT (LC)	1050 (2)	0.7BF–0.3PT (R and T)
0.75BF–0.25PT	24	0.75BF–0.25PT (LC)	1050 (2)	0.75BF–0.25PT (R and T)
0.8BF–0.2PT	24	0.8BF–0.2PT (LC)	1000 (2)	0.8BF–0.2PT (R)
0.9BF–0.1PT	24	0.9BF–0.1PT (LC)	850 (2)	0.9BF–0.1PT (R)
BF	24	BF (LC)	790 (2)	$BiFeO_3$ (R)

LC = low crystalline perovskite, R = rhombohedral perovskite, T = tetragonal perovskite.

In this work the optimization of the mechanochemical conditions for the synthesis of the whole $x\mathrm{BiFeO_3}$–$(1-x)\mathrm{PbTiO_3}$ multiferroic system has been carried out. Three different milling approaches have been compared with the ceramic method. The optimized parameters in the mechanochemical process are the atmosphere and the material of the milling medium and they are discussed and reported in increasing effectiveness order. Also, the obtained phases have been characterized from the structural point of view.

2. Material and methods

Different compositions of the system $x\mathrm{BiFeO_3}$–$(1-x)\mathrm{PbTiO_3}$ were prepared from a stoichiometric mixture of analytical grade Bi_2O_3, Fe_2O_3, PbO and TiO_2, for x = 0, 0.1, 0.2, 0.3, 0.4, 0.5, 0.6, 0.625, 0.65, 0.675, 0.7, 0.75, 0.8, 0.9 and 1. Initial mixtures were homogenized by hand in an agate mortar. The samples were synthesized by two different routes: solid state reaction and mechanochemical method. In the case of the mechanical treatment, different conditions were investigated until the synthesis optimization, two different types of vessels: an 80 cm^3 steel one and another 250 cm^3 tungsten carbide; and two different atmospheres: air and oxygen. The mechanical treatments were carried out in a planetary mill (Fritsch Pulverisette 6) and the grinding vessel was rotated at 300 rpm during different times, depending on the sample. Three types of milling approach were used. For two of them, about 4 g of the homogenized mixture of the oxides were treated in the steel vessel with five steel balls, 2 cm in diameter and 35 g in weight each, resulting in a powder:ball mass ratio of 1:44, in two different atmospheres: air and oxygen. For the third, the milling of about 10 g of the mixture of the starting oxides was carried out in the tungsten carbide vessel in air, with seven tungsten carbide balls 2 cm in diameter and 63 g in weight each (powder:ball mass ratio 1:44). In all the cases the mechanosynthesized powders were thermal treated at increasing temperatures for 2 h each, from 400 °C up to the melting point and no cumulative thermal treatments were carried out.

The classical solid-state reaction was carried out by thermal treatments at increasing temperatures from 400 °C up to 1050 °C, maintaining each temperature for 12 h; cooled by quenching, weighed, reground and examined by X-ray diffraction before the next annealing, up to the obtaining of the single phase or melting of the sample.

The phase evolution during the mechanical treatment and after each thermal treatments of the different compositions has been investigated by X-ray diffraction method (XRD) with a Bruker AXS D8 Advance diffractometer between 13° and 60° (2θ), with 2θ increments of 0.05° and counting time of 1.5 s per step. The Cu Kα doublet (λ = 0.15418 nm) was used in all the measurements.

The morphology of the samples was examined by field emission scanning electron microscopy (FE-SEM, FEI Nova NanoSEM 230 operating between 5 and 15 kV) equipped with an OXFORD INCA 250 electron dispersive X-ray detector (EDX) and transmission electron microscopy (TEM, CM20 FEG Philips working at 200 kV) for the samples with smaller particle size.

3. Results and discussion

3.1. Traditional ceramic route

Table 1 summarizes the synthesis conditions for different members of the $x\mathrm{BiFeO_3}$–$(1-x)\mathrm{PbTiO_3}$ system and Fig. 1 shows the XRD patterns of the final products obtained for each composition. The final temperature of the synthesis depends on the composition. It is possible to observe that only the compositions far from the MPB were obtained as well-crystallized phases by this method, while the compositions belonging or close to the MPB are constituted by a mixture of low crystalline perovskites. Moreover, traces of secondary phases ($Bi_2Fe_4O_9$ or $Bi_{25}FeO_{40}$) appear in the synthesis of $BiFeO_3$-rich compositions. These secondary phases are not detected when low temperatures methods are employed [25]. For these reasons, alternative synthesis methods need to be investigated in order to obtain crystalline and single phases.

3.2. Mechanochemical activation route

The mechanochemical method has been used in this work as an alternative to synthesize the BF–PT system. In order to isolate

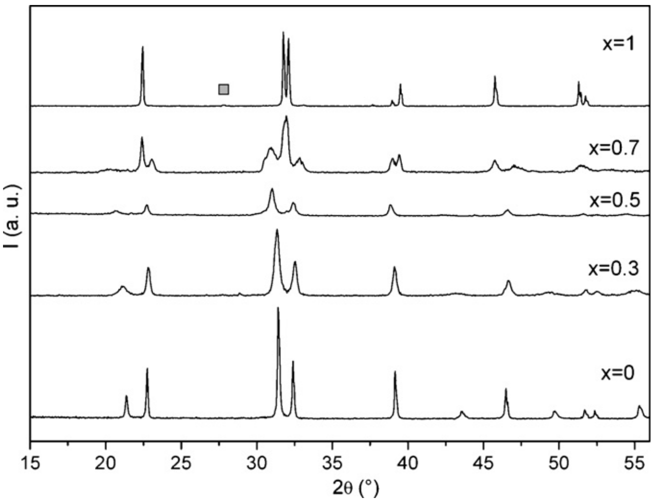

Fig. 1. XRD patterns of the different xBiFeO$_3$–(1 − x)PbTiO$_3$ phases obtained by the ceramic route at the final temperature (■ : $Bi_2Fe_4O_9$ and $Bi_{25}FeO_{40}$ secondary phases).

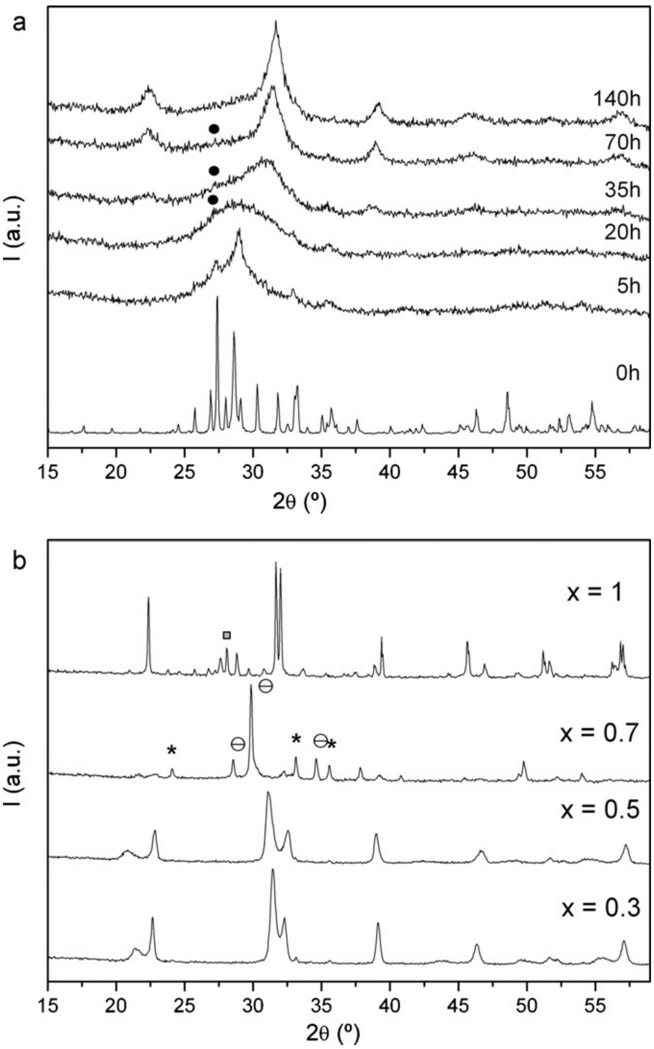

Fig. 2. (a) XRD patterns of the evolution with milling time for 0.5BiFeO$_3$–0.5PbTiO$_3$ in a steel vessel. (b) XRD patterns of the different xBiFeO$_3$–(1 − x)PbTiO$_3$ phases obtained by mechanochemical treatment in a steel vessel for 70 h and subsequently thermally treated at 800 °C (■ : $Bi_2Fe_4O_9$ and $Bi_{25}FeO_{40}$ secondary phases, ⊖: $Bi_2Ti_2O_7$ phase, ●: Bi metal and *: reactants).

single phases and to optimize the process, different conditions were employed (Table 1).

The first approach was carried out with steel vessels and air atmosphere; the results are shown in Fig. 2. In this case, the mechanosynthesis of perovskite phases was only succeeded for x values up to $x = 0.5$, while mechanoactivated and almost amorphous products were obtained for the remainder compositions. Fig. 2a shows the evolution with milling time for the 0.5BiFeO$_3$–0.5PbTiO$_3$ composition. In this figure, it is possible to observe the apparition of a weak peak ($2\theta \sim 27^\circ$) corresponding to a secondary phase that seems to crystallize in the early stages of the mechanochemical treatment. Moreover, at this milling time, a black metallic-like powder appears in the mixture, which is attributed to the presence of metallic Bi. It is possible to find in the literature works about the reduction of Bi_2O_3 during milling processes in presence of others active metals. For example, Hasanpour et al. [26] describe the formation of nanoparticles of Bi due to the fact that Fe strongly reduces Bi_2O_3 with regards to a negative enthalpy ($\Delta H = -58.5$ kJ/mol), associated with $Bi_2O_3 + 2Fe \rightarrow 2Bi + Fe_2O_3$ reaction. In order to obtain the crystalline perovskite phases, subsequently thermal treatments were needed (Fig. 2b). Different behaviours were observed for the compositions in the BF-rich, MPB and PT-rich regions. In the case of the BF-rich composition, the secondary phases ($Bi_2Fe_4O_9$ or $Bi_{25}FeO_{40}$) appeared when the thermal treatments were carried out. For the composition in the MPB ($x = 0.7$), the perovskite phase could not be isolated from the mechanoactivated mixture, and $Bi_2Ti_2O_7$ pyrochlore phase, together with the initial reactants were obtained. Finally, for compositions belonging to the PT-rich region, up to $x = 0.5$, as mentioned above, the mechanosynthesis of the pseudocubic perovskite was observe (Fig. 2a). The thermal treatments of the mechanosynthesized powders produce an increase of the crystallinity and allow the typical splitting corresponding to the tetragonal phase to be detected.

Due to the poor results obtained by the application of this approach, especially for the high BF contents, probably due to the reduction of Bi, the mechanical treatment was carried out using an O_2 atmosphere with the same steel vessels and balls. Comparing the results of the two reaction atmospheres, the evolution of the mechanochemical activation of the mixtures in O_2 atmosphere (Fig. 3a) was very similar to the mechanoactivation in air, except for the possibility of avoiding the formation of Bi metal in the early stages of milling. However, when the subsequent thermal treatments were carried out (Fig. 3b), the observed results were clearly improved (Table 1). This can be observed in Fig. 3b for $x = 0.7$, the composition in the MPB region. In this case, the perovskite type oxide was isolated after the heating, resulting in the coexistence of tetragonal and rhombohedral perovskite phases. In the case of the BF composition the synthesis was also improved, however traces of reactants are still observed, so the synthesis process is not finished, even increasing the temperature of the subsequent annealing up to the melting point. It is possible to state that the use of O_2 atmosphere in the mechanochemical process contributes favourably to the synthesis of the BF–PT system, decreasing the formation of secondary phases and the reduction of the Bi_2O_3.

It is well known that long mechanochemical reaction times or high rotation speed in steel medium could allow the contamination by the incorporation of Fe [21]. For this reason in order to increase the effectiveness of the milling without produce any contamination, and to try to complete the mechanosynthesis for all the compositions, vessel and balls made with harder and denser material were employed. The tungsten carbide was chosen as milling medium, so the mechanical impacts were more energetic and effective. Moreover, no contamination with W is confirmed by EDX. In this case, the whole system was mechanosynthesized, as it can be observed in Fig. 4a. These results show that the mechanochemical method carried out in air, with a tungsten carbide vessel,

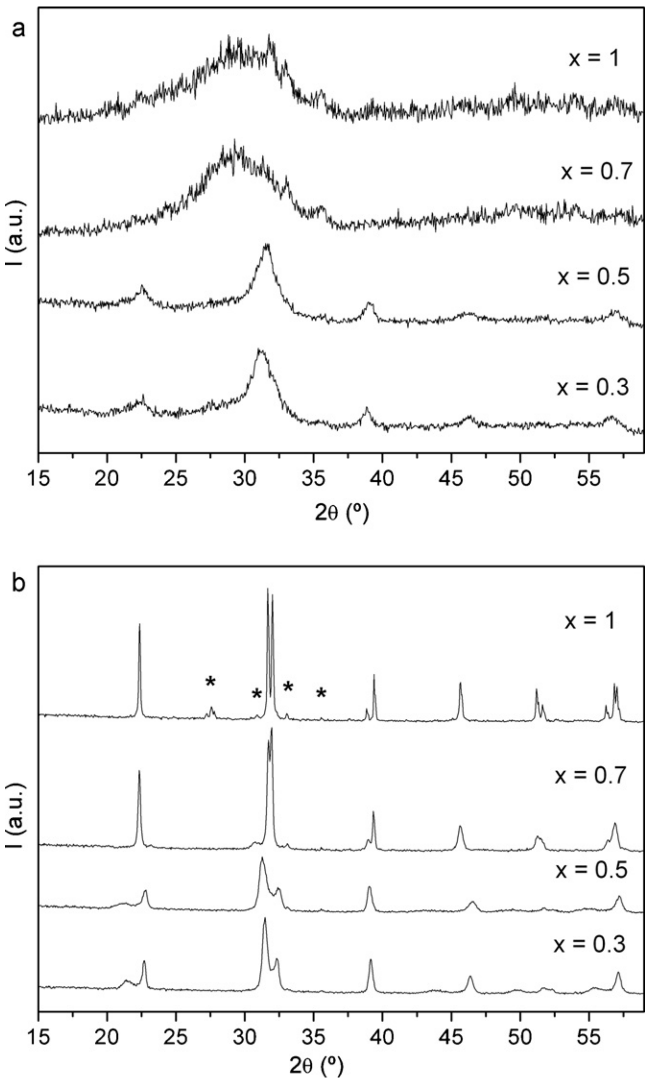

Fig. 3. XRD patterns of the different xBiFeO$_3$–(1 − x)PbTiO$_3$ compositions (a) milled in a steel vessel with oxygen atmosphere for 70 h and (b) subsequently thermally treated at 800 °C (*: reactants).

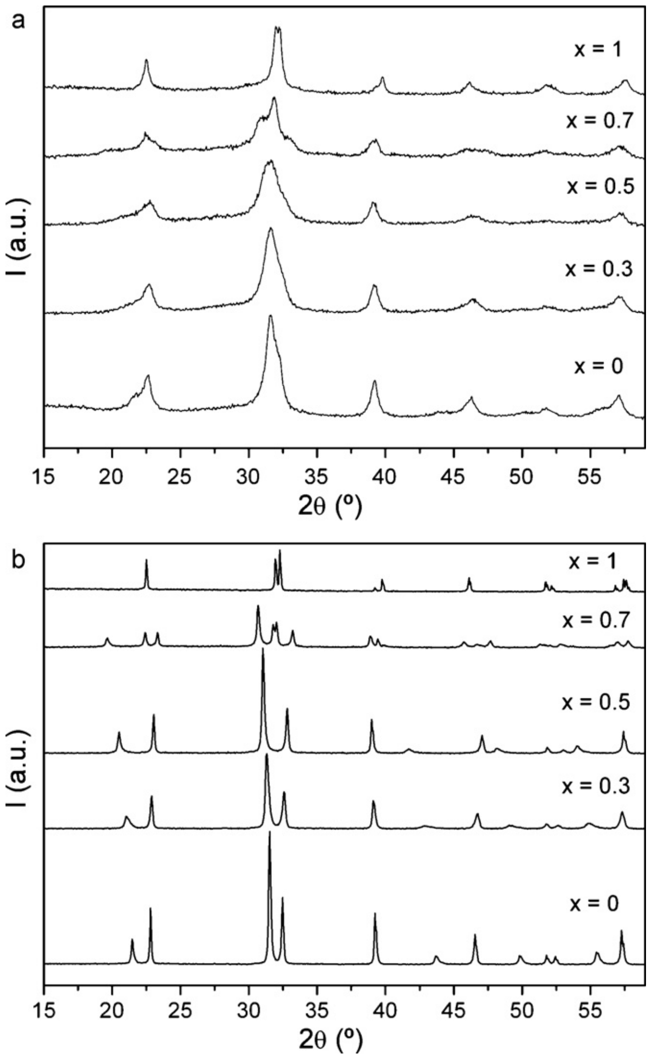

Fig. 4. XRD patterns of the xBiFeO$_3$–(1 − x)PbTiO$_3$ phases obtained by (a) mechanosynthesis in a tungsten carbide medium for 24 h and (b) subsequently thermally treated at the final temperature.

allows the xBiFeO$_3$–(1 − x)PbTiO$_3$ single phases to be obtained. The broad diffraction lines in the XRD patterns are due to the small particle size of the mechanosynthesized powders, as it can be observed in the micrographs of Fig. 5. SEM image (Fig. 5a) shows that the samples are constituted by agglomerates of fine crystals. TEM micrography (Fig. 5b) depicts these fine particles with an average crystal size of 30 nm. Subsequent thermal treatments at different temperatures were carried out to observe the crystallographic evolution and to improve the crystallinity of the powders. At the final temperature of crystallization the system is clearly distributed in three regions (Fig. 4b): the BF-rich compositions with rhombohedral symmetry; the MPB, with the coexistence of both rhombohedral and tetragonal polymorphs; and the PT-rich compositions, tetragonal. In the bibliography, as mentioned above, the localization of the MPB in a range of compositions is not clearly established yet [9]. In the present work, as it is shown in Table 1, this region can be located between the compositions with $x = 0.625$ and 0.75.

Finally, by the way of an example of the influence of the synthesis method on the morphology of the powdered perovskites, Fig. 6 shows the SEM images of the single phase BiFeO$_3$ prepared by different routes. The BiFeO$_3$ prepared by the ceramic route (Fig. 6a) is constituted by crystals of several microns, while mechanosynthe-

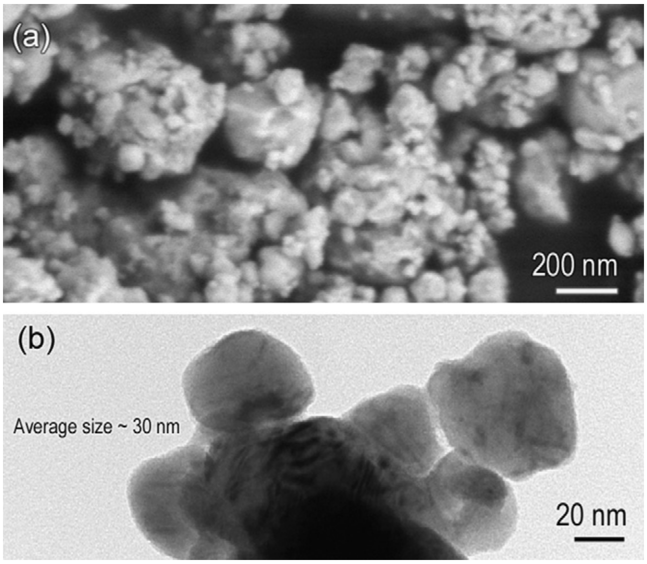

Fig. 5. (a) Scanning and (b) transmission electron microscopy images of the 0.7BiFeO$_3$–0.3PbTiO$_3$ composition obtained by mechanosynthesis in a WC medium.

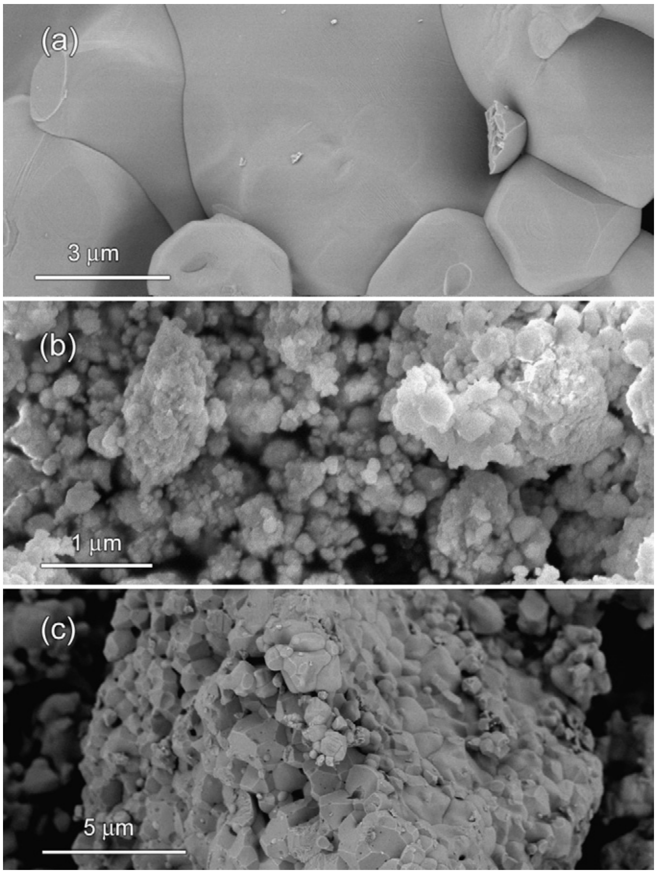

Fig. 6. Scanning electron micrographs of $BiFeO_3$ synthesized by: (a) ceramic method; (b) mechanosynthesis in WC medium and (c) mechanosynthesis (in WC medium) and annealed at 800 °C.

sized $BiFeO_3$ (Fig. 6b) is constituted by agglomerates of nanometric particles, as it has been shown for the 0.7BF–0.3PT phase (Fig. 5). As expected, after thermal annealing at 800 °C, there are important changes in the morphology of the nanosynthesized samples and larger crystals (still submicrometric) with defined facets can be observed (Fig. 6c).

4. Conclusions

The high-energy ball milling, in air, with tungsten carbide vessel and balls is the optimum approach to mechanosynthesize the whole $x BiFeO_3–(1 - x)PbTiO_3$ solid solution. By using this method it is possible to obtain nanocrystalline single phases of all compositions of the system, and their crystallinity can easily increase with a subsequent thermal treatment. Moreover, by this method it is possible to locate the MPB region between the compositions with $x = 0.625$ and 0.75.

Finally, although the mechanoactivation in a steel medium is not optimum to synthesize these perovskites, the using of oxygen atmosphere limits the reduction of the starting bismuth oxide, during the milling process, and the formation of secondary phases.

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