Metastable nature of donor-doped BiFeO$_3$ obtained by mechanochemical synthesis

Mara S. BERNARDO,*†**, Teresa JARDIEL,* Marco PEITEADO*** and Amador C. CABALLERO*

*Department of Electroceramics, Instituto de Cerámica y Vidrio (CSIC), 28049 Madrid, Spain
**POEMMA-CEMDATIC, ETSI Telecommunicación (UPM), 28040 Madrid, Spain

Nb$^{5+}$ or W$^{6+}$ donor-doped powders were synthesized by applying a mechanochemical synthesis route, in an attempt to improve the multiferroic properties of BiFeO$_3$ based materials. The as-synthesized samples evidence a highly efficient incorporation of Nb$^{5+}$ or W$^{6+}$ into the BiFeO$_3$ perovskite lattice, together with a low presence of secondary phases. The relatively high purity of the mechanochemically synthesized products is even more appealing when it is compared with the multiphase scenario obtained by a mixed oxides route for these compositions. This confirms this technique as a good alternative to conventional solid state processing; however the thermal evolution of the as-prepared powders also reveals a metastable nature of the synthesized phases which upon an external energy input leads to an unwelcome multiphase system.

Key-words : Multiferroics, BiFeO$_3$, Nanoparticles, Mechanosynthesis, Transmission electron microscopy

1. Introduction

Multiferroic materials have received increasing interest in the last few years because the coexistence of electric and magnetic ordering provides extra degrees of freedom in the storage process, thereby simplifying the operation of current device structures and/or offering novel architectures. In particular, single phase BiFeO$_3$ is one of the most promising multiferroic candidates since it may exhibit both ferroelectricity and antiferromagnetism at room temperature. However, the synthesis of BiFeO$_3$ is tricky and the obtained materials typically present a certain amount of secondary phases, which eventually degrade the multiferroic response. The modification of the BiFeO$_3$ perovskite-type structure with small amounts of different ions at the A or B positions is one of the strategies most commonly resorted to reduce the formation of parasitic phases, as well as to decrease the leakage current of BiFeO$_3$ materials and provide them with a net magnetic moment. Thus, finding out which are the most favorable dopants for improving the BiFeO$_3$ multiferroic properties has become a matter of highest interest. It has been described that rare earth dopants may stabilize the BiFeO$_3$ phase and decrease the amount of secondary phases when replacing some Bi$^{3+}$ cations at the A positions of the perovskite structure; however such dopants would also diminish the electric polarizability of the A positions. Alternatively, the use of transition ions for substituting the Fe$^{3+}$ cations at the B positions has been explored and actually there is a certain agreement (not free of controversy) about the decreasing of the electrical conductivity upon substitution with donor dopants. In this context several publications can be found reporting the enhancement of the ferroelectric properties upon doping with donors like Ti$^{4+}$ or Zr$^{4+}$, However, the number of published works concerning doping BiFeO$_3$ with higher valance-state species such as Nb$^{5+}$ or W$^{6+}$ is much lower.

Although promising improvements in the functional properties of BiFeO$_3$ thin films doped with Nb$^{5+}$ or W$^{6+}$ have been reported, generally speaking it is still not clear how stable is the BiFeO$_3$ phase in presence of these donor dopants and in some cases the equilibrium condition again implies materials containing a high amount of unwelcome secondary phases. One feasible way to overcome the possible thermodynamic restrictions is to produce the BiFeO$_3$ doped materials by alternative processing methods which may endorse metastable scenarios. Among the several possibilities, high energy mechanochemical milling has been proposed as one of the most appropriate methods to synthesize some ferroelectric materials that are not easily produced by other processing routes. Accordingly, experiments have been recently reported describing the use of mechanochemical synthesis to prepare single-phase BiFeO$_3$ nanoparticulate powders with apparently no parasite phases and promising multiferroic performances. In this contribution we have applied this high-energy milling synthesis route to the obtaining of Nb$^{5+}$ and W$^{6+}$ donor-doped BiFeO$_3$ materials. Moreover, a thorough and systematic study is presented which pays special attention to the thermodynamic stability of the as-obtained powders.

2. Experimental procedures

Ceramic powders with BiFeO$_3$, BiFe$_{0.95}$Nb$_{0.05}$O$_{3.05}$ and BiFe$_{0.95}$W$_{0.05}$O$_{3.075}$ nominal compositions were synthesized by a mechanochemical route. For these purpose, the corresponding stoichiometric amounts of the oxide precursors, Bi$_2$O$_3$ (Riedel-de Haën, >99.5%), Fe$_2$O$_3$ (Fluka, >99%), Nb$_2$O$_5$ (Fluka, >99.5%) and WO$_3$ (Alfa Aesar, >99.8%) were weighed and subjected to high energetic milling in a carbon-tungsten container with 7 balls of the same material (2 cm in diameter). With a powder-to-balls mass ratio of 17:1, all the experiments were performed at 350 r.p.m. through subsequent intervals of 20 min of milling separated by 10 min of repose, this being necessary to avoid the heating of the powder as a consequence of the ball impacts. The thermal evolution of the obtained powders was analysed by calcining
some selected samples at temperatures between 650 and 750°C during 2 h, with heating and cooling rates of 3°C/min.

The as-mechanosynthesized powders and the calcined products were structurally characterized by X-ray diffraction (XRD) in a Bruker D8 Advance diffractometer using Cu Kα radiation. The scans were collected between 20 and 60°, in steps of 0.02° with a counting time of 1.5 s per step. For the determination of the unit cell parameters the selected diffractograms were refitted by using the FullProf software[2] in the LeBail method. The morphological features were analyzed by high-resolution scanning electron microscopy (HRTEM) in a JEOL 2100F microscope operating at 200 kV and equipped with a field-emission electron gun. Energy-dispersive X-ray spectroscopy (EDS) microanalyses were collected with acquisition times shorter than 60 s to prevent the crystallization of the samples under the electron beam (see further discussion).

3. Results and discussion

The phase evolution of the undoped BiFeO₃, BiFe₀.₉₅-W₀.₀₅O₃.₀₇₅ and BiFe₀.₉₅Nb₀.₀₅O₃.₀₅ nominal powders during the mechanochemically induced reactions was followed by XRD on samples milled during different times. For the undoped composition [Fig. 1(a)] the system essentially evolves through the formation of an intermediate Bi₂₋Fe₃O₉ sillenite compound and it is only after 36 h milling when, apparently, a single-phase BiFeO₃ is obtained. Under these conditions, all diffraction peaks match with the rombohedral R3c phase of BiFeO₃ (ICDD File Card No. 71-2494). Agreeing with the work by Perejón et al.[31] these results indicate that the process is mainly controlled by the diffusion of the Bi³⁺ ions into the Fe₂O₃ particles, and greatly differs from a powder obtained by conventional solid state processing. For example, no formation of the secondary iron-rich Bi₂Fe₄O₉ mullite intermediate is ever observed on the XRD analyses of this undoped powder. At first glance this could be a quite significant result since, as we had previously reported, in samples produced by the solid state route the crystallization of the mullite phase is a critical step which stops the BiFeO₃ formation and leads to a multiphasic product.[7]

For the niobium-modified composition the phase evolution is similar to that of the undoped system and, again, 36 h milling seem to yield a pure BiFeO₃ phase. [Fig. 1(b)]. Interestingly, the secondary phases typically monitored during the solid-state synthesis of Nb-doped BiFeO₃ materials, namely the Bi₁₋Fe₂O₇ mullite and/or the Nb–Fe–Bi–O pyrochlore,[2₉,3₃] are not observed in the X-ray diffractograms of the mechanochemically synthesized powders.

The situation for the tungsten-modified BiFeO₃ powder however differs from the previous two [Fig. 1(c)]. Now, the Bi₁₋Fe₂O₇ mullite phase crystallizes after the first 6 h in the mill and also a second intermediate is formed, the Bi₁₋W₂O₂₇ phase. This last Bi–W compound, whose presence indeed explains the formation of the Fe-rich mullite due to the deviation in the stoichiometry, was observed to be decisive in the solid state preparation of W-doped BiFeO₃, leading to a multiphasic product.[2₅] But the point here is that, in contrast to what we observed for the solid state samples, the Bi₁₋W₂O₂₇ phase does evolve with further milling time and eventually an almost pure perovskite phase is obtained after 96 h.

So, according to the preliminary XRD analyses for each of the three studied powders there is an optimum milling time which apparently allows the obtaining of a pure or an almost pure BiFeO₃ phase: 36 h for the undoped and the Nb-doped compositions and 96 h for the W-doped one. Further characterization will be from now on related to just those optimum samples. A closer look to the X-ray diffractograms of these doped samples shows a noticeable shift of the (202) and (214) peaks towards lower angle. Figure 2 first shows the refinement conducted on
the corresponding XRD patterns to calculate the variation in the cell parameters of the perovskite lattice; the values resulting from that refinement are summarized in Table 1. As observed, when the undoped nominal composition is modified with niobium or with tungsten, the refined cell parameters show a significant distortion of the unit cell, with elongated a and b parameters and smaller c parameters. A visible increase in the respective volume cells is also produced which suggests the effective incorporation of these additives, Nb$^{5+}$ and W$^{6+}$, into the B positions of the perovskite lattice. The cell parameters of a sample with the same niobium doped nominal composition prepared by a conventional solid state method as described elsewhere$^{25}$ were also calculated.

For the W-doped material prepared by a solid-state method the overlap between the XRD peaks of BiFeO$_3$ and the copious Bi–W secondary phase$^{25}$ impedes a reliable estimation of cell parameters. Anyway, either the refined cell parameters or the massive formation of a secondary phase in which the dopant is present, evidences that the incorporation of these two dopants into the perovskite lattice by a conventional solid-state method is fairly limited, if not prevented. So, our results here come to confirm that the mecanochemical synthesis is truly an efficient method to obtain the donor-doped BiFeO$_3$ material. The crystal size was also estimated from the X-ray diffractograms using the Scherrer equation, yielding about 9, 7 and 6 nm for the undoped, the Nb-doped and the W-doped BiFeO$_3$ samples, respectively.

The morphological features of the mecanosynthesized particles obtained in the three optimum experiments were next analyzed by means of HRTEM (Fig. 3). As observed, the particles of the undoped BiFeO$_3$ composition have a variable size, from ~20 to 50 nm: while the biggest particles show nanocrystalline domains of 5–10 nm in size [Fig. 3(a)], the smallest ones appear monocristalline [Fig. 3(b)]. Thus, the size of these monocristalline domains is in good agreement with the average crystal size calculated from X-ray measurements. But moreover, all particles seem to be surrounded by an amorphous layer with a width of just a few nanometers; as described in the literature, such morphology is characteristic of mecanosynthesized BiFeO$_3$ powders.$^{27,29}$ Da Silva et al.$^{29}$ suggested that the observed amorphous layer is associated with the area where the heterogeneous processes of nucleation and growth of BiFeO$_3$ crystallites are spatially confined: during high-energy milling the reaction precursors are mixed at the molecular level and the new mecanosynthesized phase nucleates at the interfaces between the solid reactants. On the other hand, the lattice fringes observed on the monocristalline particles showed an interplanar distance of ~4.0 Å, corresponding with the (012) planes of the perovskite structure and in good agreement with the values reported in literature.$^{25}$ The atomic composition of the particles, as estimated from EDS analyses, evidenced a Bi/Fe ratio $\approx$ 1. It is worth to mention at this point that these EDS analyses were carried out with relatively short acquisition times, namely around 30 s; this is because, as a consequence of the far-from-equilibrium state of the surface shell in the mecanosynthesized nanoparticles, a prolonged exposure time (above 60 s) unavoidably promotes the crystallization of the particles under the electron beam.$^{29}$

Regarding the particles of the BiFe$_{0.95}$Nb$_{0.05}$O$_{3.05}$ nominal composition, they also show a nanometric size, evidencing as well a mixture of monocristalline areas and amorphous regions [Figs. 3(c) and 3(d)]. Although semiquantitative, the EDS analyses mostly show a composition that matches the expected BiFeO$_3$ phase nucleates. Spots were the EDS analysis were carried out are indicated on the pictures. The lattice fringes on some particles are also indicated with yellow arrows.

### Table 1. Calculation of the cell parameters of the BiFeO$_3$ perovskite phase for the three mecanosynthesized compositions (optimal milling conditions) and for the Nb-doped composition obtained by a conventional solid-state method at optimal conditions (BiFe$_{0.95}$Nb$_{0.05}$O$_{3.05}$ SS)

| Composition                  | a (Å) | c (Å) | $V$ ($Å^3$) | $R_p$ | $R_{wp}$ | $R_{exp}$ | $\chi^2$ |
|------------------------------|-------|-------|-------------|-------|----------|----------|----------|
| BiFeO$_3$                    | 5.594 | 13.88 | 376.2 (5)   | 38.6  | 26.1     | 18.89     | 1.91     |
| BiFe$_{0.95}$Nb$_{0.05}$O$_{3.05}$ | 5.62  | 13.95 | 379 (1)     | 48.1  | 29.2     | 23.98     | 1.47     |
| BiFe$_{0.95}$W$_{0.05}$O$_{3.075}$ | 5.62  | 13.81 | 377.1 (2)   | 44.1  | 27.8     | 23.24     | 1.42     |
| BiFe$_{0.95}$Nb$_{0.05}$O$_{3.05}$ SS | 5.594 | 13.896| 376.6 (5)   | 33.2  | 24.6     | 11.28     | 4.76     |
correspond to the perovskite phase, i.e. they shall be crystals of some parasitic phase. Specifically, those lattice fringes may belong to the (211) planes of the iron rich Bi$_2$Fe$_4$O$_9$ phase or even to some planes of the Nb–Fe–Bi–O pyrochlore phase (that one we observed when preparing these same samples by a solid state procedure\textsuperscript{25}). So, in other words, the HRTEM characterization of the Nb-doped BiFeO$_3$ makes evident the presence of a small fraction of secondary phases which, however, were not detected by the XRD measurements (most likely due to their nanocrystalline/amorphous character). That is to say, the mechanosynthesis processing, being definitely more effective than the solid state procedure to obtain Nb-doped BiFeO$_3$ particles, still cannot avoid the formation of some tiny amounts of secondary phases.

On the other hand, the HRTEM characterization for the W-modified BiFeO$_3$ powders clearly showed a higher degree of heterogeneity than that of the two previous compositions [Figs. 3(e) and 3(f)], this being in agreement with the presence of secondary phases already observed by XRD [Fig. 1(c)]. As deduced from the EDS analyses and the calculated interplanar distances most of the particles correspond to the BiFeO$_3$ phase; e.g. those nanoparticles in Fig. 3(e) show lattice fringes with an interplanar distance of 2.91 Å which correspond to the (104) crystallographic planes of the perovskite phase. But also particles belonging to the unreacted Fe$_2$O$_3$ were sporadically detected [see the rod-like structure and EDS analysis in Fig. 3(f)], together with a clearly higher fraction of amorphous regions. Furthermore, on proceeding to analyze the composition of these regions by EDS, their in-situ crystallization under the electron beam now lasted just a few seconds (Fig. 4), when usually, as we mentioned before, such progression occurs after 60 s of exposition time.

And, moreover, the lattice fringes of the in-situ crystallized particles indicate they belong to different phases, not just to BiFeO$_3$: the interplanar distances of 2.27 and 2.45 Å correspond to the (202) planes of the BiFeO$_3$ phase and the (022) planes of the Bi$_2$Fe$_4$O$_9$ phase, respectively, whereas the crystals showing an interplanar distance of 3.24 Å may belong either to the (312) planes of the Bi$_{14}$W$_2$O$_{27}$ phase or to the (310) planes of the Bi$_2$TiFe$_3$O$_{10}$ phase. In any case, the extremely fast crystallization of the particles of this composition, i.e. with a minimal energy input, points towards to a highly unstable character that easily leads to the formation of different phases.

Subsequently, to further analyze the thermal stability of the mechanochemically synthesized powders, samples were subjected to different thermal treatments. Fig. 5 shows the X-ray diffractograms of powders annealed at 650 and 750°C during 36 h. If compared with the X-ray diffractograms of the as-obtained powders, a pronounced increase in the crystallinity of the perovskite phase is produced for all the three compositions (narrower XRD peaks compared with those in Fig. 1). But additionally a boosted amount of secondary phases is detected after annealing. In particular for the undoped composition, Fig. 5(a), the presence of the Bi$_2$TiFe$_3$O$_{10}$ sillenite and the Bi$_2$Fe$_4$O$_9$ mullite phases is observed when the powder is heated at 650°C. These two secondary phases seem to disappear when increasing the temperature to 750°C, according to the absence of their corresponding peaks in the XRD. However they may be joined to the non-crystallized fraction of particles which leads to the wide band observed at low XRD angles. For the Nb-modified composition the thermal treatments lead to a situation in which the BiFeO$_3$ perovskite is still the major phase, but the crystallization of some secondary phases is produced as well [Fig. 5(b)]. As observed, the sillenite Bi$_2$TiFe$_3$O$_{10}$ is formed already at 650°C and when raising the temperature to 750°C two other phases can be detected too: the mullite Bi$_2$Fe$_4$O$_9$ and the Bi–Fe–Nb–O pyrochlore.  As described above, these two phases were not observed in the XRD analysis of the as-synthesized powder (Fig. 1), but their presence was indeed inferred from the corresponding HRTEM characterization. Finally, for the tungsten-modified composition the XRD diffractograms evidence that now a considerably amount of the Bi$_{14}$W$_2$O$_{27}$ phase coexist with the perovskite BiFeO$_3$ [Fig. 5(c)]. Actually, we tried annealing this powder at lower temperatures and for shorter dwell times, but the massive formation of this Bi–W phase could not be avoided in any case. So, in contrast with the other studied compositions, with the addition of tungsten the thermal treatment lead to a multiphase system in which the BiFeO$_3$ is no longer the main phase. Besides, higher heating temperatures (750°C) also lead to the crystalliza-
tion of the mullite phase, as well as to some crystallization of Fe₂O₃. Thus, results again indicate a low stability of the mechasynthesized W-doped BiFeO₃ powder.

In the case of the niobium modified composition the situation may seem different since the proportion of secondary phases after annealing is still relatively low. Even though, when monitoring the evolution of the cell parameters from the as-synthesized powders to the heat treated samples (see Table 2) a proven evidence of the low thermal stability of the Nb-doped BiFeO₃ particles is also found. First, for the undoped BiFeO₃ composition the cell volume remains invariable in spite of the thermal treatment (V ≈ 376 Å³). Thus, in global terms we can presume that the annealing process is not affecting the equilibrium of oxygen vacancies and related defects of the perovskite structure, i.e. by just annealing the samples the lattice parameters of BiFeO₃ are not expected to shift. However for the Nb donor-doped material, the cell volume, which was initially larger in the as-synthesized powder (V ≈ 379 Å³ due to the effective Nb⁵⁺ incorporation upon milling), now undergoes a sizeable decrease with the heating supply (V ≈ 376 Å³). Since, as mentioned, by itself the thermal treatment produces no changes in the equilibrium defects of the BiFeO₃ structure, the observed shifting in the cell volume for the Nb-doped material actually indicates that with such prolonged thermal treatment a fraction of the previously incorporated niobium segregates out from the perovskite lattice. This ultimately confirms that the donor-doped phases obtained through the mechasynthesis process have a metastable nature which should not be ignored for further processing these ceramic powders. For instance, for preparing Nb or W-doped BiFeO₃ bulk ceramics one would have to take into account that the working window will be even narrower than for the undoped system. Nevertheless, the donor-doped powders here obtained through the mechasynthetic route seem promising for their deposition in form of thin films on substrates which favour the BiFeO₃ crystallization through epitaxial growth and, hence, may aid to maintain the doped perovskite structure in the final materials.

Table 2. Calculation of the cell parameters of the BiFeO₃ perovskite phase for the as-synthesized and the thermally treated powders of undoped and Nb-doped BiFeO₃ nominal compositions

| Composition          | a (Å)     | c (Å)   | V (Å³)  | R₂p | Rwp | Rexp | χ² |
|----------------------|-----------|---------|---------|-----|-----|------|----|
| BiFeO₃               | 5.594 (4) | 13.88 (1) | 376.2 (5) | 38.6 | 26.1 | 18.89 | 1.91 |
| BiFeO₃,Nb₀.₁₅O₁.₅₅  | Heated (750°C) | 5.5927 (6) | 13.899 (2) | 376.48 (9) | 31.8 | 20.5 | 10.96 | 3.49 |

4. Conclusions

The mechasynthetic procedure has been successfully applied to the production of Nb- and W-doped BiFeO₃ powders through reaction pathways that are different to those observed during the solid-state synthesis. Nanoparticles and nanocrystalline domains are obtained which evidence an efficient incorporation of Nb⁵⁺ or W⁶⁺ into the BiFeO₃ perovskite lattice. Although an exhaustive characterization by HRTEM also shows the presence of some tiny amounts of non-crystallized parasitic phases, our results confirm that this synthesis technique is undeniably more efficient than a conventional solid state routine to prepare BiFeO₃ ceramic powders with high donor-doping levels and very low percentages of secondary phases. However, we have observed as well that the as-synthesized powders display a metastable nature meaning that an external input of energy promotes the formation of unwanted multiphasic products, especially for the W-modified composition. Obviously, this certitude should be contemplated in a further processing of the ceramic powders and/or for possible applications at high temperatures.

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