Synthesis, microstructure and properties of BiFeO$_3$-based multiferroic materials: A review

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BiFeO$_3$-based materials are currently one of the most studied multiferroics due to their possible applications at room temperature. However, among the large number of published papers there is much controversy. For example, possibility of synthesizing a pure BiFeO$_3$ phase is still source of discussion in literature. Not even the nature of the binary Bi$_2$O$_3$-Fe$_2$O$_3$ diagram has been clarified yet. The difficulty in controlling the formation of parasite phases reaches the consolidation step. Accordingly, the sintering conditions must be carefully determined both to get dense materials and to avoid bismuth ferrite decomposition. However, the precise conditions to attain dense bismuth ferrite materials are frequently contradictory among different works. As a consequence, the reported properties habitually result opposed and highly irreproducible hampering the preparation of BiFeO$_3$ materials suitable for practical applications. In this context, the purpose of the present review is to summarize the main researches regarding BiFeO$_3$ synthesis, microstructure and properties in order to provide an easier understanding of these materials.

Keywords: BiFeO$_3$, synthesis, sintering, ferroelectric properties, magnetic properties.

1. MULTIFERROIC MATERIALS

By definition single phase multiferroic materials are those that simultaneously present at least two of the so-called “ferroic” properties: ferroelectricity, ferromagnetism and ferroelasticity [1]. These properties lie in the presence of an electric polarization, magnetization or elastic deformation that can be switched hysterically by the action of an electric field, a magnetic field or stressing, respectively. Recently, the multiferroic term has been extended to materials with other magnetic orders like ferrimagnetism or antiferromagnetism [2] and even to a ferrotoroid order [3, 4].

Magnetoelectric multiferroics are one of the most interesting categories of multiferroic materials. In this kind of materials the coexisting properties of ferroelectricity and ferromagnetism (or ferrimagnetism or antiferromagnetism) are also coupled. This coupling, known as magnetoelectric effect, gives place to extra degrees of freedom which may allow magnetization to be switched by an electric field and polarization to be switched by a magnetic field [2, 6, 7] (figure 1.a). Coexistence of ferroelectricity and ferromagnetism can, but need not lead to magnetoelectric coupling and actually only a subgroup of the multiferroic materials fulfills this condition (figure 1.b). In practice, magnetoelectric coupling can be achieved directly or indirectly via strain. In the first case, application of an electric field changes the local symmetry of the magnetic cations and, hence, changes their spin orientation. In the case of indirect coupling, change in local symmetry occurs due to the effects of strain. [2]. Indirect coupling gives rise to the preparation of composites with magnetoelectric coupling. As an example, the combination of a piezoelectric material intimately connected to a magnetoelastic material may lead to an indirect multiferroic behavior via strain.
Magnetoelectric materials can be used for typical applications of ferroelectric and ferromagnetic materials. However, their most potential applications are those derived from the possibility of switching magnetization under an electric field and vice versa. Thus, the extra degree of freedom provided by the magnetoelectric effect gives rise to new applications such as electromagnetic resonance devices controlled by electric fields, transducers with tunable piezoelectricity or, even most attractive, devices for memory storage [4, 8, 9]. Commercial magnetic memories use a magnetic field for writing information with two magnetic states (+M and −M) that represent magnetic bits “0” and “1”. With the aim to protect the information the magnetic memories usually consist in hard magnetic materials that require a high coercive field. However this means high energy consumption and low writing speed. From this point of view it is currently considered that writing directly by an electric field may solve these shortcomings and, hence, this possibility, still in progress, have become the main driving force in multiferroic materials research.

Multiferroic materials can be divided into two general groups: single-phase multiferroics and composites or two-phase multiferroics. Single-phase multiferroics are those in which at least two “ferroic” properties are presented within the same phase. Instead, composites are multiphase systems in which each phase presents a different “ferroic” property. As previously mentioned, in composite multiferroics magnetoelectric coupling occurs indirectly via strain. According to their phase distribution there are different kinds of composite multiferroics and, actually, reports can be found in which an enhancement of several orders of magnitude in the magnetoelectric coupling respect to single-phase systems is described [2, 4]. However, a single-phase multiferroic with a strong coupling between its ferroelectric and its ferroelectric orders could allow an easier control of the magnetic nature through electric fields. Unfortunately, the number of known single-phase multiferroic materials is not very high.

The first material simultaneously showing ferroelectricity and ferromagnetism, the nickel iodine boracite Ni₃B₇O₁₃I, was discovered in 1966, [10]. That was followed by the synthesis of several multiferroic boracites, all of them with very complex structures and many atoms per unit cell. However, in spite of its incalculable value to proof the multiferroic concept, their practical applications are unavoidably hampered by their complex structures [11]. Subsequently the search for other magnetoelectrics began in Russia based on the idea of replacing the B cation of the perovskite-type ferroelectric phase for other cations with magnetic order. However, all these initial attempts again failed in obtaining a simultaneous ferroelectric and ferromagnetic with response within the same phase. It is not till the beginning of the 21st century when new improvements in understanding the phenomena implied in the simultaneous coexistence of magnetic and ferroelectric orders [11], together with novel synthesis methods and characterization techniques, have given rise to a renaissance in the field [5]. In year 2000 Nicola A. Hill [11] reported that the scarcity of multiferroic materials must be attributed to intrinsic factors since the requirements for symmetry and electric properties might be contradictory. From the point of view of symmetry there are 31 point groups that allow an electric polarization and 31 that allow a spontaneous magnetization, but only 13 point groups are found in both categories. However, the most exclusive requirements are those that deal with the electronic configuration. The presence
of d electrons is necessary for the existence of a magnetic moment (and consequently for any kind of magnetic order), but at the same time the occupation of this d orbitals tends to reduce the crystallographic distortion which is necessary for ferroelectricity. For example in PbTiO$_3$ and BaTiO$_3$ both ferroelectric compounds showing a perovskite-type structure, the Ti$^{4+}$ ions have a d$^0$ electron configuration. This electronic state facilitates the Ti 3d - O 2p hybridization which is essential for stabilizing the ferroelectric distortion [12]. On the other hand, the occupancy of the d-orbitals undergoing a Jahn–Teller distortion which, becoming the dominant effect, will decrease the centrosymmetric distortion required for ferroelectricity [11]. In other words, alternative mechanisms may explain the concurrent existence or ferroelectricity and magnetic order in magnetoelectric materials and, actually, reports can now be found which explore the possibilities of non-oxidic systems such as the K$_3$FeF$_6$ or Pb$_5$Cr$_3$F$_{19}$ families [13, 14].

The case is that at present there are few known families of oxide materials that exhibit multiferroic behavior. The family of REMnO$_3$ (RE$^{3+}$Mn$^{3+}$O$_2^+$), where RE is a rare-earth ion from Pr$^3+$ to Lu$^3+$ (although it can also be Y$^3+$ and Bi$^{3+}$) [15-17], is one of these systems displaying concurrent magnetic and ferroelectric order, although at temperatures below 30-40 K. Compounds belonging to this family have two low-temperature phase transitions. The nature of the first transition is not completely understood while the second one is simultaneously a magnetic and a ferroelectric phase transition [18]. In the particular case of the terbium manganite, TbMn$_2$O$_5$, it has been observed a highly reversible switching of the electrical polarization with moderate magnetic fields, ~ 0.2 T, but at the same time the occupation of this d-orbitals undergoes a Jahn–Teller distortion which, becoming the dominant effect, will decrease the centrosymmetric distortion required for ferroelectricity [12]. On the other hand, the family of REMnO$_3$ (RE$^{3+}$Mn$^{3+}$O$_2^+$) manganites can crystallize in the orthorhombic and the hexagonal symmetry (depending on the size of the RE$^{3+}$ cation), but only those that show the hexagonal symmetry belonging to the spatial group R3c (α-BiFeO$_3$) has also been proposed that the space group P1 could be more appropriate than the well accepted polar space group R3c to describe the structure of α-BiFeO$_3$ at room temperature [26].

2. BiFeO$_3$ STRUCTURE

At room temperature and atmospheric pressure, BiFeO$_3$ shows a rhombohedrally distorted perovskite structure belonging to the special group R3c (α-BiFeO$_3$ phase). Unit cell parameters are $a_{\text{eq}} = 3.965$ Å and $c_{\text{eq}} = 89.3 – 89.4$. The BiFeO$_3$ unit cell can be also described in the hexagonal symmetry where $a_{\text{eq}} = b_{\text{eq}} = 5.58$ Å and $c_{\text{eq}} = 13.90$ Å [22]. Another important structural parameter is the rotation angle of the oxygen octahedral, related with the Goldschmidt tolerance factor for perovskites (t). For BiFeO$_3$, t tolerance factor is 0.88 so the oxygen octaedra must buckle in order to fit into a too small cell [22] resulting in a Fe-O-Fe angle (θ) value of 154-156° [22].

In some particular cases certain discrepancies have been found regarding the crystal structure of α-BiFeO$_3$ at room temperature. As an example, in crystals with a lower grain size than 30 nm it has been observed a progressive change from rhombohedric to cubic symmetry [24]. In the case of epitaxial BiFeO$_3$ films different structures have been suggested such as rhombohedral, tetragonal and monoclinic [20, 25]. Recently, it has also been proposed that the space group P1 could be more appropriate than the well accepted polar space group R3c to describe the structure of α-BiFeO$_3$ at room temperature [26].

![Figure 3. BiFeO$_3$ magnetic structure showing the origin of the G-type antiferromagnetic order (adapted from [1]) (a), the formation of the weak magnetic moment (adapted from [1]) (b) and the spin cycloid superstructure (adapted from [29]) (c).](image-url)


SYNTHESIS, MICROSTRUCTURE AND PROPERTIES OF BiFeO$_3$-BASED MULTIFERROIC MATERIALS: A REVIEW
Ferroelectricity in BiFeO₃ is originated from the stereochemically active lone-pair orbital of bismuth ions (6s²), which being largely displaced with regards to the FeO₆ octahedra, generates a spontaneous polarization along the [111] axis of the rhombohedral unit cell [1, 27]. On the other hand, BiFeO₃ is a G-type anti-ferromagnet [22, 29] (figure 3.a) in which all neighboring magnetic spins are oriented antiparallel to each other. As a consequence of the oxygen octahedral distortion, directly related with the Fe-O-Fe angle, BiFeO₃ structure presents spin canting which results in a weak magnetic moment in the unit cell according with Dzyaloshinskii-Moriya interaction [1, 29] (figure 3.b). However, this net magnetic moment exhibits a long-range superstructure consisting on a spin cycloid with a 64-nm wavelength (figure 3.c) that is incommensurable with the crystallographic structure [29, 30]. The result is that, for single-crystals with size fairly larger than the spin cycloid, the net magnetization is zero which, at first, prevents a magnetoelastic effect. The magnetoelastic effect may be recovered by frustration of the spin cycloid. As it will be described later, this can be achieved by different methods.

At temperatures around 370 °C a second order phase transition is produced which has been assigned to the transition from anti-ferromagnetic to paramagnetic structure of BiFeO₃ [22, 31, 32]. This magnetic transition is associated with anomalous lattice expansion [32]. Around 825 °C a first order transition is produced from the paramagnetic α-BiFeO₃ phase to the high temperature phase β-BiFeO₃ [33]. This first order transition is accompanied by an abrupt decrease of the unit cell volume [32, 34, 35] as well as abrupt changes in atomic positions [32]. Besides, this transition is also accompanied by a maximum in the dielectric constant assigned to the transition from ferroelectric to paraelectric [34]. On the other hand, the symmetry of the β-BiFeO₃ phase has been subject of much controversy in literature. Nevertheless, most of authors agree that it is centrosymmetric [22, 32, 35-37] corroborating that the phase transition at 825 °C is the ferroelectric to paraelectric transition. In 2008, Hamount et al. [36] reported that β-BiFeO₃ shows a monoclinic symmetry belonging to the spatial group P2₁/m with a monoclinic angle of 90.01°. However, Palai et al. [35] proposed that β phase is orthorhombic, although with some coexistence of rhombohedral domains. In any case these authors were unable to establish the spatial group of this phase from their experimental data. On the other hand, in the same year Selbach et al. [32] suggested that β phase is rhombohedral, belonging to the spatial group R(-3) m. This assertion is not accepted by other authors which state that the transition at 825 °C could not be ferroelastic (as it is inferred from the changes in the ferroelastic domains configuration) if the symmetry of both the α and the β phases is rhombohedral [22, 35]. The reasons for these contradictions can be found on the difficulty for obtaining a pure BiFeO₃ phase and the complexity associated with sample characterization. On one hand, the presence of secondary phases complicates the structural characterization of the paraelectric phase [32, 35]. On the other hand, X-Ray diffraction technique has a poor sensitivity to the positions of the oxygen atoms as a consequence of their low electronic density compared with that of bismuth or iron atoms [22]. In this sense, high temperature neutron diffraction is a much more illustrating technique. So, based on this last characterization technique, Arnold et al. [37] asserted that β-phase symmetry is orthorhombic although with some phase coexistence, as had been proposed earlier [35]. In fact, in 2010 Selbach et al. [38] rectified their first proposal of a rhombohedral symmetry [32] to accept the orthorhombic symmetry proposed by Arnold et al. [37].

At higher temperature, around 933 °C, a second order phase transition from β to γ phase of BiFeO₃ has been reported to occur [35], although this transition is not considered intrinsic by some other authors [33]. For this high temperature phase a cubic symmetry belonging to the space group Pm(-3)m has been suggested [35]. Besides, it has been observed that the transition from the β phase with orthorhombic symmetry to the γ phase with cubic symmetry is accompanied with a sharp decrease of the band-gap towards zero, indicating that at this temperature the transition from an electric insulator to a metallic behavior is produced [35].

3. EQUILIBRIUM PHASES IN THE Bi₂O₃-Fe₂O₃ SYSTEM

The first phase diagrams for the Bi₂O₃-Fe₂O₃ system were published in the mid-60’s [39]. Years later, modifications to these initial diagrams were published [33, 35, 36, 40, 41] (figure 4), although with certain discrepancies between them. For example, in some diagrams [33, 40, 41] the α-Bi₂O₃ → γ-Bi₂O₃ phase transition is also extended to the compatibility region between Bi₁₋ₓFeₓO₃ (or Bi₁₋ₓFeₓO₃₋₀) and BiFeO₃ phases, which is considered by other authors [35] as an indication of a non equilibrium state. In the same way, subtle differences can be found on the temperature at which a liquid phase first appears (from 745 °C [40] to 792 °C [41]), on the temperature at which the BiₓFe₁₋ₓO₃ decomposes (from 934 °C [41] to 961 °C [35]), as well as on the temperature for the BiFeO₃ peritectic decomposition (from 852 °C [33] to 934 °C [41]), this latter more noticeable. Moreover, according to Palai et al. [35] the peritectic decomposition of BiFeO₃ occurs from the γ phase, but this phase is not considered as thermodynamically stable by other authors [33]. Attempts to explain these discrepancies attribute them to an uncontrolled level of impurities and to
the presence of defects in the as-prepared samples [33], but also to data being collected under non-equilibrium conditions [35]. Although in the phase diagrams there is one point of agreement, the BiFeO$_3$ phase being thermodynamically stable in a wide range of temperatures, the case is that controversy remains open and contradictory data that question both the diagram and the stability itself of the BiFeO$_3$ phase are currently being published.

Actually many works in the specialized literature claim the difficulty in obtaining a pure BiFeO$_3$ phase and the unfeasibility to avoid the presence of secondary phases [40, 42-45]. According to the phase diagrams, slight deviations from the stoichiometric composition would result in a mixture of BiFeO$_3$ and Bi$_2$Fe$_4$O$_9$ phases if we move to Bi$_2$O$_3$ rich compositions or in a mixture of BiFeO$_3$ and Bi$_2$Fe$_4$O$_9$ if we move to the Fe$_2$O$_3$ rich area, but it would be possible to obtain a pure BiFeO$_3$ with a careful stoichiometric control. Furthermore, the coexistence of the three phases in an equilibrium state has been as well reported [43], although according to the Gibbs phase rule this situation is in fact incompatible for a binary system. Based on this idea Valant et al. [43] suggested that in the presence of tiny amounts of impurities, the Bi$_2$O$_3$-Fe$_2$O$_3$ system behaves as a pseudo-binary system: slight deviations from the nominal composition will considerably increase the proportion of secondary phases, particularly if impurities are incorporated into the Bi$_2$Fe$_4$O$_9$ bismuth-rich phase (the corresponding phase field in the phase diagram would significantly narrow).

On the other hand, some other authors assert that bismuth ferrite is actually a metastable phase [44, 45], so under certain conditions it will decompose to yield the secondary Bi$_2$Fe$_4$O$_9$ and Bi$_{25}$Fe$_{39}$O$_{74}$ phases according to reaction 1:

\[
49 \text{BiFeO}_3 \rightarrow 12 \text{Bi}_2\text{Fe}_4\text{O}_9 + \text{Bi}_{25}\text{Fe}_{39}\text{O}_{74} \quad [1]
\]

Again, the conditions at which BiFeO$_3$ decomposes are source of discussion. For example Morozov et al. [40] stated that BiFeO$_3$ decompose at temperatures higher than 780 °C. On the contrary, Carvalho et al. [44] avowed that BiFeO$_3$ decomposes at temperatures below 600 °C, being possible to obtain a pure phase with a fast cooling that avoids its decomposition. In 2009, by means on high temperature X-ray diffraction measurements Selbach et al. [45] asserted that BiFeO$_3$ is metastable from 447 up to 767 °C. In this range of temperatures the Bi$_2$Fe$_4$O$_9$ and Bi$_{25}$Fe$_{39}$O$_{74}$ secondary phases would have a slightly higher stability than BiFeO$_3$. Thus, the pure BiFeO$_3$ phase could be obtained at temperatures slightly higher than 767 °C, with a fast heating to avoid the initial formation of Bi$_2$Fe$_4$O$_9$ and Bi$_{25}$Fe$_{39}$O$_{74}$ phases and a fast cooling to avoid the decomposition of the BiFeO$_3$ reacted phase. Due to the small Gibbs energy difference between the BiFeO$_3$ and the decomposition products (Bi$_2$Fe$_4$O$_9$ and Bi$_{25}$Fe$_{39}$O$_{74}$) minor variations may shift the equilibrium of the BiFeO$_3$ formation/decomposition reactions (reaction 2):

\[
12 \text{Bi}_2\text{Fe}_4\text{O}_9 + \text{Bi}_{25}\text{Fe}_{39}\text{O}_{74} \rightleftharpoons 49 \text{BiFeO}_3 \quad [2]
\]

For example, in consonance with the proposal by Valant et al. [43] the presence of impurities with a larger solubility in the Bi$_2$Fe$_4$O$_9$ or Bi$_{25}$Fe$_{39}$O$_{74}$ secondary phases than in the BiFeO$_3$ may increase the stability range of these secondary phases shifting the equilibrium of reaction 2 towards the left.

4. SYNTHESIS OF SINGLE-PHASE BiFeO$_3$

4.1. Mixed oxides synthesis

BiFeO$_3$ compound was for the first time synthesized in Russia by the mid 50’s, using the conventional mixed oxides synthesis method [46]. Around that time, different authors reported that BiFeO$_3$ could be synthesized by the solid state reaction of Bi$_2$O$_3$ and Fe$_2$O$_3$ precursors at temperatures around 700 and 800 °C with annealing times from 30 to 120 min. However, in 1967 Achenbach et al. [42] pointed out the difficulty of obtaining a pure BiFeO$_3$ phase. According to these authors all attempts to obtain pure BiFeO$_3$ result in multiphase products in which BiFeO$_3$ comes together with small amounts of parasite phases. Furthermore, modifications in the temperature, time or atmosphere of the annealing treatment, repeated firing and grinding or even the addition of small amounts (< 0.5 mol %) of a third component did not ever lead to a pure BiFeO$_3$ phase. These authors also reported that at temperatures below 700 °C the formation reaction of BiFeO$_3$ is incomplete, at temperatures between 700 and 750 °C BiFeO$_3$ formation competes with the Bi$_2$Fe$_4$O$_9$ secondary phase formation and, finally, at temperatures above 750 °C BiFeO$_3$ becomes unstable and decomposes. In view of these impediments Achenbach et al. suggested a method to obtain a pure BiFeO$_3$ phase without secondary phases which is still used nowadays by many research groups [26, 47]. This method lies in shifting the nominal composition towards a composition with a certain Bi$_2$O$_3$ excess. According to the phase diagrams, firing such composition at temperatures around 750 °C leads to a mixture of BiFeO$_3$ plus unreacted Bi$_2$O$_3$. Finally this Bi$_2$O$_3$ excess can be lixiviated by leaching with concentrated HNO$_3$ resulting in a pure BiFeO$_3$ phase to the X-ray diffraction characterization.

In 2003 Morozov et al. [40] asserted that the solid-state synthesis of a pure BiFeO$_3$ is not viable due to the fact that its decomposition temperature is lower than its activation one. Not much later Wang et al. [48] suggested a new method to obtain a pure BiFeO$_3$ phase. This method, so-called “rapid liquid phase sintering”, consists in the thermal treatment of the oxide precursors at high temperatures (880 °C) during a brief period of time (450 s) and applying extremely fast heating and cooling rates (100 °C/s). These authors claim that the presence of a liquid phase (the thermal treatment takes place at temperatures above the melting point of Bi$_2$O$_3$), together with the fast heating rate, efficiently accelerate the formation reaction of BiFeO$_3$ phase and prevent the secondary phase formation. Following Wang et al.’s publication this rapid liquid phase sintering method has been frequently employed by different authors to synthesize BiFeO$_3$ apparently free of secondary phases [49, 50]. For example Pradhan et al. [49] have studied the effect of slight variations in the annealing conditions concluding that the temperature must be exactly 880 °C in order to obtain a pure phase; lower temperatures (850 °C) lead to an incomplete reaction, whereas higher temperatures (slightly higher: 890 °C) render multiphase products as a consequence of the Bi$_2$O$_3$ volatilization. On the other hand Yuan et al. [50] analyzed the influence of the particle size of the precursor powders. These authors realized that working with Bi$_2$O$_3$ or Fe$_2$O$_3$ of an average particle size > 1 µm impedes the formation reaction to be completed and again results in a final product with small amounts of secondary phases.
However the obtaining of a pure BiFeO$_3$ phase by the rapid liquid phase sintering method of Wang and co-workers was later questioned by other authors, mostly because on those works the presumption of a pure BiFeO$_3$ phase is just based on a rough characterization just by means of X-ray diffraction (a technique that actually shows low sensitivity to phases composed by relatively lighter elements, like the iron rich Bi$_2$Fe$_4$O$_9$ phase). In particular in 2007 Valant et al. [43] evidenced that the conventional solid-state process may lead to a BiFeO$_3$ phase in the XRD patterns as pure as that obtained through the liquid phase sintering method. However, when going to the scanning microscope appreciable amounts of secondary phases are easily detectable in both cases. Actually this lack of rigorous characterization is still found in many current works reporting a pure BiFeO$_3$ phase, probably explaining the mentioned discrepancies. But besides, the work of Valant and co-workers also suggested that, since the coexistence of three phases in equilibrium is incompatible with a binary system (Bi$_2$O$_3$-Fe$_2$O$_3$), the secondary phases are stabilized by trace levels of impurities whose presence cannot be easily controllable during the synthesis process. Only by using extremely pure reagents (≥ 99.9995 %) a pure BiFeO$_3$ phase was attained by these authors after annealing at 800 °C during 5 hours. In any case, although the effect of impurities is certainly accepted, some groups still stand up for the metastability of the BiFeO$_3$ phase [35, 45, 51].

But, as mentioned before, another strategy that has been exploited in order to facilitate the synthesis of BiFeO$_3$ by a mixed-oxides route entails the addition of small amounts of a third component. These additives could substitute the Bi$^{3+}$ or Fe$^{3+}$ cations at the A or B positions of the perovskite structure and, hence, can contribute to stabilize the BiFeO$_3$ with respect to the secondary phases. And, what is more, the addition of external dopants may as well be helpful to improve the magnetoelectric properties of the synthesized product. Thus, it has been described in the literature that rare earth dopants like La$^{3+}$ [52, 53], Gd$^{3+}$ [52, 54], Nd$^{3+}$ [52], Sm$^{3+}$ [52, 55], Y$^{3+}$ [56], or Ho$^{3+}$ [57] may have the desired effect of stabilizing the BiFeO$_3$ phase and decreasing the amount of secondary phases when replacing some Bi$^{3+}$ cations in the A positions of the perovskite structure. However, these dopants may diminish the electric polarizability of the A positions [52, 58, 59], so alternatively the use of transition ions like Mn$^{2+}$ [60] or Ti$^{4+}$ [61-63] for substituting the Fe$^{3+}$ cations in B positions, has been recently proposed. Nevertheless, the addition of a third component must be taken cautiously since in many cases they can have the contrary effect stabilizing one of the secondary phases (or both of them) [63-66], with an analogous result to that described by Valant et al. [43].

4.2. Synthesis by chemical routes

In order to get a pure BiFeO$_3$ avoiding byproducts of secondary phases, chemical synthesis routes have been widely used. One of them is co-precipitation synthesis [67-72] which lies in the simultaneous precipitation of different elements at certain pH and concentration conditions. A subsequent thermal annealing leads to the chemical reaction between the co-precipitated hydroxides to get the final complex oxide. Co-precipitation synthesis represent two main advantages with regards to the mixed-oxides method: a lower contamination probability and a higher reactivity [73]. Therefore, this method improves the reaction kinetics minimizing impurities that could stabilize the secondary phases.

Several authors assert that it is possible to obtain a pure BiFeO$_3$ by a co-precipitation synthesis method [67, 68, 70, 71]. However, the precise conditions to avoid the formation of secondary phases are in some cases contradictory. For example, whereas Ko et al. [68] upheld that a bismuth excess is required to compensate volatilization during annealing, both Liu et al. [70] and Chen et al. [67] argue that it is possible to obtain a pure BiFeO$_3$ by starting from the stoichiometric composition. On the other hand, according to Shami et al. [71] a pure BiFeO$_3$ single phase will be obtained by co-precipitation route if Bi$_2$O$_3$ is used as the Bi$^{3+}$ precursor instead of the generally used Bi(NO$_3$)$_3$.5H$_2$O. However, once again most of these publications lack of an accurate characterization (merely XRD) so any conclusion must be observed cautiously.

Besides co-precipitation, other chemical routes such as sol-gel, the Pechini method or the like have as well been considered in order to prepare a pure BiFeO$_3$ phase. In some cases these methods seem successful in order to obtain BiFeO$_3$ nanoparticles [74-78], but divergences are also frequent. Actually it has been suggested that the BiFeO$_3$ obtained by these wet chemistry routes evidences a metastable behavior and under certain conditions - again contradictory [44, 68]- it decomposes leading to secondary phase byproducts.

Another chemical strategy which has been recently studied to synthesize BiFeO$_3$ pure phase is the hydrothermal (or solvothermal) processing. Actually during the past decades hydrothermal processing has become a very attractive method for the synthesis of advanced materials due to its intrinsic benefits like a high compositional and morphological control as well as a high purity of the obtained powders by avoiding subsequent annealings or milling treatments [79]. Accordingly, in 2006 Han et al. [80] and Chen et al. [81] reported the obtaining of micron-sized particles of pure BiFeO$_3$ by applying a hydrothermal route. However, once again the lack of a thorough characterization of the obtained products questions the inexistence of secondary phases. The case is that slight variations in the temperature, pressure and/or pH parameters resulted in the formation of secondary phases and, even, in obtaining only some other phases of the Bi$_2$O$_3$-Fe$_2$O$_3$ system, such as Bi$_{12}$Fe$_{0.63}$O$_{18.945}$ or Bi$_2$Fe$_4$O$_9$ [80]. In 2007 Wang et al. [82] achieved the synthesis of spherical BiFeO$_3$ nanoparticles by addition of a small amount of KNO$_3$. According to these authors small changes in the experimental conditions can also lead to the formation of different phases. For example, when using LiNO$_3$ instead of KNO$_3$ as mineralizer a pure Bi$_{13}$Fe$_{0.63}$O$_{39.69}$ phase is obtained [83]. However, it has been also reported that using potassium salts as precursors may result in BiFeO$_3$ crystals that contain K$^+$ cations incorporated into the perovskite structure [84]. But after these early works, the current research regarding the hydrothermal synthesis BiFeO$_3$ is mainly focused on understanding the mechanisms implied in the hydrothermal reaction [85], the effect of systematic variations in the experimental conditions [86, 87], the effect of quelants or surfactants [88-91], the crystal growth mechanisms [87, 90] and/or the obtaining of BiFeO$_3$ particles with tailored morphology [87, 90].

Furthermore, it has also been reported that the microwave-assisted hydrothermal approach gives a considerable
improvement in crystallinity and purity of the obtained BiFeO₃ samples with respect to the traditional hydrothermal processes [92-94]. However, the specific conditions in which a pure BiFeO₃ phase is obtained are again contradictory among different works. Some authors report that the use of the adequate mineralizer (either KOH [92] or NaOH [94]) under a short reaction time lead to a pure BiFeO₃ phase according to the XRD characterization whereas others defend that a N₂ or a H₂ atmosphere is required in order to obtain pure BiFeO₃ ceramics by this method [95].

4.3. Mechanochemical synthesis

One additional method currently used for preparing pure BiFeO₃ powders is the mechanochemical synthesis. This method allows the obtaining of different crystalline oxides within one step, also avoiding subsequent thermal annealing. In many cases, products obtained by this method are nanoparticles with a high sinterability. However, the main advantage of this method is the possibility to obtain metastable phases which are tricky to obtain by other conventional synthesis methods [96].

In 2007 Szafraniak et al. [97] reported the synthesis of BiFeO₃ particles by a mechanochemical route at room temperature. The obtained product consists of irregular agglomerates of nanoparticles of ~50 nm in size. HRTEM characterization shows that nanoparticles present a core-shell structure with crystalline BiFeO₃ as a core and an amorphous shell of 1-2 nm thick. Similar results have been more recently obtained by Da Silva et al. [98]. These authors have proven the high reactivity of the amorphous shell, concluding that these areas play a key role in the mechanically induced chemical reactions. Besides, the mechanochemical synthesis of BiFeO₃ doped in A positions with different ions such as Eu³⁺ [99], Sm³⁺ [100], Sr²⁺ [101]; of BiFeO₃ co-doped in A and B positions with Ba²⁺ and Mn²⁺ respectively [102], as well as of complex systems comprising BiFeO₃ and other perovskite structures such as PbTiO₃ [103] or BaTiO₃ [104] has also been studied.

5. FABRICATION OF DENSE BiFeO₃ BULK MATERIALS

Sintering is the consolidation step of the ceramic material during which energy is provide to the system in order to activate different physical and chemical processes that lead to particle joining and porosity releasing. Sintering also drastically changes the functional microstructure of the ceramic material which, in fact, is closely related to its properties [73, 105]. Densification of bismuth ferrite is tricky and materials with a density not higher than 90 % of the BiFeO₃ theoretical density are usually obtained. The high porosity content in BiFeO₃ materials is a severe impediment for most practical applications. During sintering, both grain growth and densification occur simultaneously. Thus, equilibrium between these two processes – that are usually competitive – will have a key influence on the microstructure of the final material [73]. Generally speaking, it is necessary to find a sintering temperature and time regime in which the mechanisms involved in densification prevail over those involved in grain coarsening. In the particular case of BiFeO₃ materials, these problems with densification must be added to the above mentioned synthesis complexity and thermal stability of this compound, so making the sintering step even more critical.

As mentioned, rapid liquid phase sintering is a method frequently used to obtain BiFeO₃ materials [48-50, 106]. In the Bi₂O₃-Fe₂O₃ system, annealing at temperatures above ~ 775 °C may result in the formation of a Bi-rich liquid phase [35]. So, at these conditions, sintering will be influenced or even controlled by the presence of the liquid phase. If this liquid suitably wets and covers the surface of the solid particles then it may provide a high diffusivity path to matter transport [105]. In order to create a liquid phase during the sintering of BiFeO₃ materials, the stoichiometry must be slightly enriched in bismuth; alternatively, the material may have compositional heterogeneities with Bi-rich areas. Typically when using this sintering method the liquid phase formation is achieved by conducting both the synthesis and the sintering processes in one single step, taking the reactants to high temperatures at a rapid heating rate [48]. Even though, the obtained density values are still not higher than 92 % of the BiFeO₃ theoretical density [48, 50]. Besides, due to the presence of the liquid phase an undesired exaggerated grain growth may not be avoided when using this method [49]. As an example, micrographs of materials obtained by this method are shown in figure 5.

Figure 5. Scanning electron micrographs of BiFeO₃ ceramics (polished (a) and chemically etched (b) surfaces) sintered at 850 °C in presence of a Bi-rich liquid phase that lead to an exaggerated grain growth.

Furthermore, the high temperature during sintering may also result in a loss of stoichiometry as a consequence of bismuth volatilization. These problems are usually avoided by using a Bi-excess in the nominal composition [68] as well as by covering the sample with powders of the same composition and running the thermal treatment in a closed crucible [107, 108].

Recently the use of spark-plasma sintering (SPS) has been tested as an alternative way to improve the densification in BiFeO₃ bulk materials [47, 109, 110]. This sintering method is quite useful to promote the densification mechanisms without leading crystal growth [109, 111]. Density values around 96 % of the theoretical density have already been reported for BiFeO₃ ceramics prepared by SPS [47, 109]. However, although in some of the published works a pure BiFeO₃ phase is detected by X-ray diffraction [109], the corresponding SEM micrographs do show rests of liquid phase that suggest the presence of secondary phases.

5.1. Defect chemistry in BiFeO₃ materials

For a complex oxide like BiFeO₃, the punctual defects that must be considered are the creation of cationic or anionic vacancies, the stoichiometric deviations and the changes in the oxidation states of Fe³⁺ or Bi⁵⁺ cations.
At first instance, the possible volatilization of Bi$_2$O$_3$ during the thermal treatment may result in a loss of stoichiometry, giving rise to the formation of either Fe-rich phases or the appearance of bismuth and oxygen vacancies ($V_{Bi}$ and $V_{O}$, respectively) in the BiFeO$_3$ structure. This can be expressed in terms of the Kröger-Vink notation according to reaction 3:

$$2 \text{Bi}_n^+ + 3 \text{O}_n^- \rightarrow 2 \text{V}_{Bi}^{\text{\textasciitilde}} + 3 \text{V}_{O}^{\text{\textasciitilde}} + \text{Bi}_2\text{O}_3$$  \[3\]

Besides, the presence of bismuth vacancies may result in the occupation of the empty A sites by iron cations, leading to non-stoichiometric samples with (Bi$_{1-x}$Fe$_x$)FeO$_3$ composition as proposed by Morozov et al. [40]. In addition to this, it has been also proposed that as a consequence of the thermal treatment Fe$^+$ cations may reduce its oxidation state from III to II [48]. This would result in Fe$^+$ ions at the B-sites of the perovskite structure and will lead to oxygen vacancies in order to reach the charge neutrality (reaction 4):

$$\text{Fe}_n^{\text{\textasciitilde}} \rightarrow \text{Fe}_n^{\text{\textasciitilde}} + 1/2 \text{V}_{O}^{\text{\textasciitilde}}$$  \[4\]

The presence of Fe$^{\text{\textasciitilde}}$ ions in BiFeO$_3$ materials has been widely studied [47, 93, 95, 112-115] considering that it may have a key role in the electromagnetic properties. In this sense, although analyses on BiFeO$_3$ single crystals by X-ray photoemission spectroscopy (XPS) has just detected iron in the 3+ oxidation state [112], more recent studies through Mössbauer spectroscopy [93] point towards the presence of a small amount of Fe$^{\text{\textasciitilde}}$ in low spin configuration in BiFeO$_3$ ceramic powders. Actually the fluctuations in the oxidation state of iron cations can be promoted by applying a gas flux (air, O$_3$, N$_2$, or Ar) during the thermal treatment [47, 95, 115]. For example, Kumar et al. [115] reported that an Ar flux during processing BiFeO$_3$ ceramics by a sol-gel method can modify the Fe$^{\text{\textasciitilde}}$/Fe$^{\text{\textasciitilde}}$ ratio as well as the proportion of secondary phases (their amount seems to decrease when compared to ceramics obtained under an air flux).

5.2. Obtaining of doped BiFeO$_3$ bulk materials

The addition of dopants to BiFeO$_3$ materials (with the aim of stabilize the perovskite phase and/or modify its properties) can have a noticeable effect in both the densification and microstructural development during sintering.

As described in the literature the grain growth during sintering can be inhibited through the addition of dopants as La$^{3+}$ [108], Sm$^{3+}$ [116], Zn$^{2+}$ [65], Pb$^{2+}$ [117], Nb$^{5+}$ [63, 118] or Ti$^{4+}$ [61, 62]. Grain growth control by the effect of a third component is in fact very common in polycrystalline ceramics. In general, there are two mechanisms by which grain growth could be inhibited: the pinning and the solute drag effects. The pinning effect is produced when small particles of a secondary phase are pinned onto the grain boundaries, thereby restricting the diffusion processes that cause grain growth. On the other hand, the solute-drag effect is produced when the dopant (also called solute) is segregated to the grain boundaries due to a low solubility on the host component. Located at the grain boundaries, this solute slows down the diffusion resulting in an inhibition of grain growth [73] (Figure 6). On the other hand when doping with aliovalent cations -those showing a different oxidation state that the cation to substitute- defects will be formed in order to neutralize the charge excess introduced by the dopant. In the case of acceptor dopants, the substitution will introduce an excess of negative charge. This can be compensated by different defect reactions, like creation of oxygen vacancies [119] or oxidation of pre-existing Fe$^{\text{\textasciitilde}}$ ions to Fe$^{\text{\textasciitilde}}$ [117]. In contrast, in case of donor dopants, the substitution will introduce an excess of positive charge. This charge can be compensated through reduction of Fe$^{\text{\textasciitilde}}$ to Fe$^{\text{\textasciitilde}}$ [114, 120], annihilation of oxygen vacancies [121] or creation of Bi$^{3+}$ or Fe$^{3+}$-cationic vacancies [122]. These defects may also affect the grain growth [61, 62].

6. PREPARATION OF BiFeO$_3$ THIN FILMS

From the point of view of microelectronics applications, the obtaining of materials in the shape of thin films is a key point. Typically the layer thickness must lie from a few fractions of nanometers up to cents of nanometers. As a result the material will have a strong interaction with the substrate, implying great changes in processing and properties compared with bulk materials. For example, as previously explained, the crystalline structure of bismuth ferrite can shift from rhombohedral to orthorhombic in epitaxial BiFeO$_3$ thin films [20]. Besides, such interaction with the substrate may also originate preferential orientation, stress or texturation.

In order to obtain BiFeO$_3$ thin films, different deposition methods have been employed. Among those based on physical evaporation techniques, pulsed laser deposition (PLD) and sputtering are the most used. In these techniques, atoms are ejected from a solid target material due to bombardment with energetic ions that are obtained from plume plasma which is generated in the sputtering chamber after applying an rf alternating current, a magnetic field or a laser beam. During the deposition the different experimental parameters – atmosphere and pressure of deposition, time of deposition or target composition – must be controlled. In this sense several works that study the optimal conditions for obtaining highly crystalline BiFeO$_3$ thin films using these methods [123-125] can be found in the literature. However, the problems related with the presence of secondary phases and heterogeneities seem to be persistent. For example Ternon et al. [123] were unable to obtain films which were free of parasitic phases and showed a dense and homogeneous microstructure at the same time. Lee et al. [124] studied the effect of deposition time in the crystallization and properties of films deposited on Pt/Ti/SiO$_2$/Si(100) substrates. These authors observed that the increase in thickness after long deposition times was...
accompanied by a decrease in the relative amount of Bi$_2$O$_3$ secondary phase (which was only observed at the interface with the substrate). Qui et al. [125] studied the differences between applying high temperatures during the deposition stage or applying a subsequent thermal annealing. According to these authors the microstructure displays a higher density in the first case, although the deposited layer does not present suitable ferroelectric properties. The influence of substrates in thin films prepared by sputtering has also been studied concluding that substrates like SrRuO$_3$ [126, 127] or LaNiO$_3$ [128] favor the BiFeO$_3$ crystallization.

With regards to the chemical deposition methods, the most common are chemical solution deposition (CSD), chemical vapor deposition (CVD), metal organic chemical vapor deposition (MOCVD), spin-coating and sol-gel. In order to obtain high quality layers by these chemical deposition methods the parameters of the deposited solution as well as the thermal annealing conditions must be controlled. For example, by carefully controlling these variables Das et al. [129] successfully prepared transparent BiFeO$_3$ films by spin-coating over glass substrates. Besides, reports can also be found in which the preparation of single-phase BiFeO$_3$ thin films is obtained through doping strategies [130, 131]. Nevertheless, in most of these works an insufficient characterization of the structure and microstructure of the films is still provided.

7. ELECTROMAGNETIC PROPERTIES IN BiFeO$_3$ MATERIALS

7.1. Electric response in BiFeO$_3$ materials

One of the most important shortcomings of BiFeO$_3$ materials regarding its possible practical applications is the high electrical conductivity that they usually present [22]. This high electrical conductivity makes impossible the polarization of the materials and, hence, hampers its use as ferroelectrics.

The ferroelectric cycles commonly described in the literature for BiFeO$_3$ materials usually indicate a high remnant polarization (Pr), although they habitually display a worrisome rounded shape [48, 49, 132] (figure 7). One example of this kind of cycles would be those published by Wang et al. [48] in a work asserting an enhancement of the polarization which has been cited more than 400 times since it was published in 2004. However, later in 2008, Scott [133] compared the cycles usually reported for BiFeO$_3$ materials with those obtained for Bi$_2$O$_3$ thin films obtained through doping strategies [130, 131]. Nevertheless, this high conductivity still persist. Some authors attribute such high conductivity values. Working with thin films Bèa et al. [135], realized that the Bi$_2$O$_3$ secondary phase can create conduction pathways through the material resulting in a high electrical conductivity. The same effect could be expected from the Bi-rich secondary phase, Bi$_5$Fe$_2$O$_{13}$, with a sillenite-type structure quite similar to that of Bi$_2$O$_3$. On the other hand, Lahmar et al. [136] deposited thin films from a BiFeO$_3$ composition containing a 10 % iron excess by spin-coating and estimated that the presence of γ-Fe$_2$O$_3$ parasitic phase was behind the observed increase in the electrical conductivity. These authors also proposed that the electrical conductivity in single-phase BiFeO$_3$ films is originated by the oxygen vacancies and it may be decreased by shifting the nominal composition either towards a 10 % Bi$_2$O$_3$ enriched composition (preexistent bismuth vacancies due to volatilization would be occupied by Bi$^{3+}$ ions, and hence O$^2-$ species would be released annihilating the oxygen vacancies) or towards compositions containing up to 5 % Fe$_2$O$_3$ excess (so Fe$^{3+}$ ions may occupy the bismuth vacancies also releasing O$^2-$ that annihilate oxygen vacancies). In contrast, Ke et al. [137] suggested that the high electrical conductivity must be ascribed to the existence of Fe$^{2+}$ ions rather than to the presence of oxygen vacancies or secondary phases (excepting the case in which these phases are present in macroscopic amounts). These authors performed a structural study on bulk BiFeO$_3$ ceramics sintered under different atmospheres (either Ar or O$_2$), and observed that the dielectric losses were higher for the ceramics sintered in Ar. Thus, by leaning on XPS analyses, these authors attributed the higher conductivity to a higher proportion of Fe$^{2+}$.

But besides when BiFeO$_3$ materials are doped in A or B positions with small amounts of different ions, significant changes can be promoted in their properties due to the effect that these dopant may have on stabilizing the α-BiFeO$_3$ phase, on the densification mechanisms and on the defect chemistry. However, once more, the literature shows a lot of controversy regarding the properties of BiFeO$_3$ doped materials. This must be attributed to the high sensitivity of BiFeO$_3$ materials to the experimental parameters during processing, but also to the...
The multiferroic properties [62]. Finally, Zr$^4+$ [144], V$^5+$ [145] or W$^6+$ [146] are other donor-like dopants which have been used to improve the ferroelectric properties of BiFeO$_3$ materials. However, in spite of the reported improvements in the dielectric properties, ferroelectric loops are still not saturated.

On the other hand, doping at the Fe$^{3+}$ positions with manganese is also very common in the literature of BiFeO$_3$ materials. Some authors suggest that small amounts of this dopant decrease the electrical conductivity of BiFeO$_3$ materials [61, 62, 121, 122], although once again some works describe just the opposite effect [139]. In fact, there is not a generalized agreement regarding the charge compensation mechanisms [61, 122, 143] in this context, it has been recently suggested that the charge compensation mechanism in Ti-doped BiFeO$_3$ ceramics may shift from an electronic compensation mechanism in the grain interior to a vacancy compensation mechanism in the grain boundary due to Ti$^{4+}$ segregation, this having a key role in the multiferroic properties [62]. Finally, Zr$^4+$ [144], V$^5+$ [145] or W$^6+$ [146] are other donor-like dopants which have been used to improve the ferroelectric properties of BiFeO$_3$ materials. However, in spite of the reported improvements in the dielectric properties, ferroelectric loops are still not saturated.

On the other hand, aliovalent dopants will strongly influence the electric properties of BiFeO$_3$ materials, as a consequence of changes in the chemistry of defects. According to Mazumder et al. [117], doping with Pb$^2+$ decreases the electrical conductivity of BiFeO$_3$ and improves its polarization by decreasing the Fe$^{3+}$ concentration. Doping with Zn$^{2+}$ [139], Co$^{2+}$ or Cu$^{2+}$ [140] has also been reported to decrease the leakage current of BiFeO$_3$ materials. However, many other works propose that the electrical conductivity of bismuth ferrite materials rises upon substitution with acceptor dopants. For example, Qui et al. [121] asserted that doping with Ni$^{2+}$ increases the conductivity by means of a vacancy conduction mechanism. According to Khomchenko et al. [119], doping with Pb$^{2+}$, Ca$^{2+}$, Sr$^{2+}$ or Ba$^{2+}$ increases the oxygen vacancy concentration—which is supported by Mössbauer spectroscopy—and thus increases the electrical conductivity. On the other hand, Mouré et al. [101] suggest that doping BiFeO$_3$ with Sr$^{2+}$ increases the grain boundary conductivity.

With regards to donor dopants there is a more generalized agreement about their effect in decreasing the electrical conductivity. For example, it has been several times reported in literature that doping with Nb$^{5+}$ decreases the electrical conductivity of BiFeO$_3$ materials [66, 118, 141]. However, the reasons for this lower conductivity of the doped material have been ascribed to different factors such as a decrease in the oxygen vacancies concentration or a possible niobium segregation at the grain boundaries. The case is that ferroelectric loops have been measured just for Nb-doped BiFeO$_3$ materials conformed as thin films and, up to date, results are contradictory. For example, whereas some works assert an enhancement of the remnant polarization contrast with undoped BiFeO$_3$ thin films prepared by similar methods [141] (although saturated ferroelectric loops are never obtained in those cases), others support that remnant polarization falls off with niobium doping [142]. Apart from niobium, doping with Ti$^{4+}$ in the Fe$^{3+}$ positions is also a common method used to decrease the electrical conductivity in BiFeO$_3$ materials [61, 62, 121, 122], although once again some works describe just the opposite effect [139]. In fact, there is not a generalized agreement regarding the charge compensation mechanisms [61, 122, 143] in this context, it has been recently suggested that the charge compensation mechanism in Ti-doped BiFeO$_3$ ceramics may shift from an electronic compensation mechanism in the grain interior to a vacancy compensation mechanism in the grain boundary due to Ti$^{4+}$ segregation, this having a key role in the multiferroic properties [62]. Finally, Zr$^4+$ [144], V$^5+$ [145] or W$^6+$ [146] are other donor-like dopants which have been used to improve the ferroelectric properties of BiFeO$_3$ materials. However, in spite of the reported improvements in the dielectric properties, ferroelectric loops are still not saturated.

Among the large amount of published works, saturated ferroelectric cycles have been occasionally reported for BiFeO$_3$ materials, both in bulk [149] and in thin films [20, 150-154]. Also the reported remnant polarization values are very variable (table I). In the case of bulk materials, the highest value reported up to date is about 12 $\mu$C/cm$^2$ [149], whereas for thin films those values are up to one order of magnitude higher [20] although the reasons for this high values are still not clear [134].

In summary, the literature of BiFeO$_3$ based materials shows plenty of results which are poorly reproducible. Thus, it is possible to find works that describe completely different properties in samples prepared with similar procedures. The
disparity in the polarization values could be due to different reasons, from a high electrical conductivity in bulk samples [21] to strain-stabilized structural modifications in thin films [20]. Nevertheless, the effect of stress on the increase of the remnant polarization in thin films has been later refused by different authors as Erenstein et al. [134] o Ederer et al. [156]. Using the modern theory of polarization, some theoretical studies allow explaining both the unexpected low values and those anomaly large which have been recently obtained considering structures in which the ions can shift their oxidation state [21].

However, these theoretical results have not been experimentally verified due to problems related with the synthesis and the characterization of the BiFeO₃ materials [21].

### 7.2. Magnetic response in BiFeO₃ materials

As previously explained, BiFeO₃ crystals with a size larger than the spin cycloid wavelength, i.e. 64 nm, show an antiferromagnetic behavior. However, this superstructure can be frustrated leading to a ferrimagnetic response, something which has been pursued by different strategies: applying high magnetic fields (∼20 T), reducing the particle size, introducing restrictions in thin films or by chemical substitution [2, 157, 158].

In 2003 Wang et al. [20] reported an extraordinary large magnetization value (M_s ~150 emu/g, i.e. ~1 μemu/g) for epitaxial BiFeO₃ thin films with a thickness of 70 nm. The authors attributed this anomalous enhancement of magnetization (which depended on the film thickness) to strain. However, years later several authors have refuted this hypothesis concluding that the magnetic response was actually independent on the film thickness [25, 134] and suggesting that the high magnetization value could be attributed to Fe²⁺ ions [134] or to small amounts of the γ-Fe₂O₃ secondary phase [25].

It has also been reported that BiFeO₃ nanoparticles smaller than ~92 nm in size show an enhancement in magnetization strongly dependent on the particle size [158-161]. This improvement in magnetization has been related with the frustration of anti-ferromagnetism in reduced size particles as well as with the presence of decompensate spins and anisotropic stresses in the surface of the nanoparticles [159].

In 2007, Mazumder et al. [158] reported a magnetization of ~0.4 μemu/Fe for BiFeO₃ nanoparticles with a size of 4 nm, a considerably high value in comparison with that obtained for bulk samples ~0.02 μemu/Fe. However, samples with similar sizes obtained through different synthesis methods yielded different magnetization and coercivity values [159, 162]. This last fact suggests that the magnetic properties of BiFeO₃ nanoparticles also depend on the processing story [162].

Chemical substitution has also been used quite frequently in order to improve the magnetization in BiFeO₃ materials. Substitution of Bi³⁺ ions in A sites by diamagnetic ions like La³⁺, Sr²⁺, Pb²⁺ or Ba²⁺ results in an enhancement of the magnetization which can be correlated with the ionic radius of the substituting dopant [119, 163]. Khomchenko et al. [119] suggested that the enlargement in magnetization when substituting with a diamagnetic dopant is due to the variation on the anisotropic constant. However, other authors support that such increase in magnetization for Ba²⁺ doped BiFeO₃ materials is due either to the increasing in the Fe²⁺ concentration when dealing with thin films [114] or to a different balance of the oxygen vacancies in the case of bulk BiFeO₃ ceramics [164].

Finally it has also been published that doping in B sites of the perovskite structure may lead to an enhancement in magnetization, since the substitution of iron atoms can increase the value of the Fe-O-Fe angle and, hence, modify the super-exchange interaction [165]. As reported, dopants like Ti⁴⁺ [61, 122, 143, 166], Nb⁵⁺ [118, 167] o Zr⁴⁺ [168] can originate a weak ferromagnetism in BiFeO₃ materials.

### 8. CONCLUSIONS

In the last decade a great effort has been done regarding the synthesis and the obtaining of multiferroic BiFeO₃-based materials. However, among the large amount of published papers there is still much controversy which is mainly due to the difficulties in preparation and characterization of BiFeO₃ materials. The published phase diagrams for the Bi₂O₃-Fe₂O₃ system show contradictory data and not even the thermodynamic nature of the BiFeO₃ phase is clear in literature. Synthesis of a pure BiFeO₃ phase is tricky and usually results in the presence of a certain amount of secondary phases. A scarce characterization may overlook the parasite phases leading to contradictory results and poorly reproducible properties. Besides, misinterpretations of the obtained data, such as ferroelectric loops typical of highly conductive materials, also frequently lead to erroneous conclusions. The result is a misunderstanding in the origin of the observed properties which, on the other hand, are habitually interesting for applications of BiFeO₃ multiferroics. Thus, works regarding BiFeO₃ materials must be critically considered with these key points in mind and taking into account their experimental procedures as well as the thoroughness of their characterization. Only in this way, practical applications of BiFeO₃ multiferroics could be reached, which is in fact a truly challenging for materials research.

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