Improved Magnetic Properties and Structural Characterizations in Mn Doped $0.9\text{BiFeO}_3\text{-}0.1\text{BaTiO}_3$ Compositions

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A structurally correlated magnetization enhancement is reported for Mn doped $0.9\text{BiFeO}_3\text{-}0.1\text{BaTiO}_3$ compounds. X-ray diffraction and Rietveld refinement studies revealed a distorted perovskite structure with the coexistence of rhombohedral and monoclinic symmetries. Mössbauer spectroscopy results showed a magnetic spectral signature of ordered Fe^{3+} ions for the rhombohedral phase of the undoped sample, and for both rhombohedral and monoclinic phases of the Mn doped samples. A significant magnetization increase (reaching 0.50 emu/g), associated to the magnetic ordering of the Cm phase and to the retention of the Mn^{3+} valence state, was observed for Mn doped samples.

Keywords: Multiferroic, BiFeO_3 , Structural Properties, Magnetism

Bismuth ferrite (BiFeO_3 ; BFO) is one of the most studied multiferroic materials, mainly due to its reported magnetoelectric properties at room temperature, potential use in nonvolatile memory applications and developments in the fundamentals of solid state physics [1,2]. BFO ferroelectric and antiferromagnetic phase transitions are found significantly above room temperature, i.e., it is a ferroelectric material below $T_c \sim 1100$ K, and an antiferromagnetic one below $T_N \sim 650$ K [3,4]. The drawbacks of BFO for bulk practical applications are the low resistivity and the difficult to synthesize single-phased polycrystalline materials. One way for overcoming these problems is the synthesis of solid solutions with other perovskite materials, such as BaTiO_3 (BT) or PbTiO_3 (PT) [5,6].

It is reported that the addition of BT in BFO leads to the releasing of the macroscopic magnetization [7,8,9] with the emergence of a weak-ferromagnetic ordering, increasing the electrical DC resistivity [10, **Error! Bookmark not defined.**] and improving the piezoelectric properties [9]. However, the increase of the electrical resistivity of BFO-BT s.s. with high concentrations of BFO ($x = 0.9$ and 0.8 , for example) is not enough for practical applications and magnetizations are very low. To overcome the low DC electrical resistivity, one solution is doping these materials with multiple valence ions [10,11]. Among them, Mn doping can be used to reduce dielectric losses and improve the piezoelectric properties of PZT based materials, for instance, and indeed have been successfully used to improve the DC resistivity and reduce the low-frequency dielectric losses in BFO-BT s.s. [12]. In this context, investigations focusing to understand the relations between the structure and the magnetic properties of BFO-BT s.s. seems to be imperative.

In this paper, structural, magnetic and Mössbauer spectroscopy studies were conducted in $0.9\text{BiFeO}_3\text{--}0.1\text{BaTiO}_3 - x \text{ wt.}\% \text{ MnO}_2$ ($x = 0, 0.3, 0.5$ and 1.0) s.s. processed by high-energy ball milling (HEBM). Our results point to the formation of perovskite structured materials with the coexistence of rhombohedral ($R3c$) and monoclinic (Cm) phases for all studied samples. The magnetizations were improved because the Cm phase, previously reported as paramagnetic [13], becomes (anti)ferromagnetic with Mn incorporation.

Polycrystalline $0.9\text{BiFeO}_3\text{--}0.1\text{BaTiO}_3$ (BFO-BT) samples were processed by HEBM in a Retsch PM 100 planetary ball mill by using analytical grade (Aldrich) bismuth oxide (Bi_2O_3), iron oxide (Fe_2O_3) and BT as starting materials, as previously reported [5, **Error! Bookmark not defined.**]. Following the batching formula, the powders were ball milled for 3 h and annealed at 1023 K for 1 h. In the resultant powder x wt.% of MnO_2 ($x = 0, 0.3, 0.5$ and 1.0) was add. The Mn doped powders were milled and annealed again in the same optimized conditions [**Error! Bookmark not defined.**]. X-ray diffraction (XRD) analyses were performed using a Shimadzu XRD 7000 diffractometer (CuK_α radiation) operating in step-like mode in the 2θ range of $20^\circ - 100^\circ$ in steps of 0.01° . The XRD results were refined through the Rietveld methods using the FULLPROF program [14]. Magnetic hysteresis loops were performed at room temperature in a homemade magnetometer. The Mössbauer spectroscopic (MS) characterizations were performed in the transmission geometry, using a conventional Mössbauer spectrometer in a constant acceleration mode. The γ rays were provided by a nominal 25 mCi ^{57}Co (Rh) source and the MS results were analyzed with a nonlinear least-square routine, with Lorentzian line shapes. The isomer shift (IS) data are given relative to $\alpha\text{-Fe}$.

Fig. 1(a) shows the XRD patterns for Mn doped BFO-BT samples, revealing that all compositions were crystallized in a pure distorted perovskite structure (see discussion below). No structural transformation was observed with the increase of Mn concentration, although a small change in the shape and a decreasing in the intensity of the peaks around 32° and 39° , Fig. 1(b), had been observed, indicating that further doping could result in structural transformations. In fact, Guo et. al [15] reported structural transformations for similar s.s. when Mn concentration is high than 2.0 wt%, with the structural symmetry changing from a rhombohedral to a monoclinic one. These structural changes are accompanied by an increase of the lattice parameters and unit cell volumes [12,16], as a direct consequence of the difference between the Mn, Fe and Ti ionic radii. In fact, the Mn ions in the MnO_2 compound are in the Mn^{4+} valence state. However, the MnO_2 precursor can be

easily converted into Mn_2O_3 at 923 K [10,11]. So, the primary manganese ions may be in the Mn^{3+} valence state once these samples were synthesized at 1123 K. The ionic radius of Mn^{3+} ions is approximately 0.645 Å, which is much lower than those of Bi^{3+} (~1.03 Å) and Ba^{2+} (~1.35 Å) ions, but very close to those of Fe^{3+} (~0.645 Å) and Ti^{4+} (~0.605 Å) ions [19]. This way, Mn^{3+} ions tend to enter into the B site of the perovskite structure, and only small changes in the lattice parameters and unit cell volumes are expected in this case, as indeed observed in XRD results for Mn doped BFO-BT s.s. (see Table I). Another transformation, which is reported to prevent the conversion of Fe^{3+} into Fe^{2+} , consequently lowering the conductivity [10], may occur as follows: $\text{Mn}^{3+} + \text{Fe}^{2+} \rightarrow \text{Fe}^{3+} + \text{Mn}^{2+}$ [10]. Thus, if Mn^{2+} ions are present they can occupy both A and B sites of the perovskite structure, once their ionic radius is approximately 0.83 Å [16], and lead to significant structural changes, as those observed by Guo et. al [15].

For investigating the structural properties of BFO-BT s.s., Rietveld refinement analyses were performed in the XRD results of $x = 0, 0.5$ and 1.0 samples, as shown in Fig. 2. The XRD peaks were indexed considering the coexistence of $R3c$ and Cm polar symmetries of the perovskite structure, by applying an $R3c-Cm$ structural model for BFO-BT s.s. **[Error! Bookmark not defined., 13]**. Furthermore, models with Mn atoms in the Mn^{2+} and Mn^{3+} valence states were also considered and tested, as well as models with Mn atoms occupying A, B or both A and B perovskite sites. The refined parameters and graphical criterion indicate that the better refinement model was reached with Mn atoms in the Mn^{3+} valence state occupying only the B site. The structural parameters are listed in Table 1 and, as expected, almost no structural changes were observed with Mn content increasing.

Fig. 3 shows the ^{57}Fe MS spectra for Mn doped BFO-BT samples. The red lines give the least square fits of the experimental spectra, while blue, brown and green illustrations are relative to the subspectra used in the fit protocol. For the undoped sample, the MS is very similar to that found for BFO [17], showing a magnetic spectral signature which corresponds to ordered Fe^{3+} ions in two

crystallographic environments with dissimilar electric field gradients [17]. This spectrum was fitted with two sextets of closer magnetic hyperfine fields ($B_{\text{HF}} = 47.5$ and 47.9 T) and very different quadrupolar splitting ($\Delta_{\text{EQ}} = -0.075$ and 0.342 mm/s) associated only with Fe^{3+} ions (isomer shifts, $\text{IS} = 0.33$ and 0.46 mm/s) [18]. In addition to these two sextets, a doublet was also used for adequately fit the MS spectrum. This doublet corresponds to a small part of the total spectrum and its Δ_{EQ} (0.521 mm/s) and IS (0.162 mm/s) parameters indicates that this subspectrum also corresponds to Fe^{3+} ions in a noncentrosymmetric paramagnetic environment.

For Mn doped samples ($x = 0.5$ and 1.0), the MS results were also fitted with two sextets that presented small differences in the magnetic hyperfine fields, i.e., $B_{\text{HF}} = 49.3$ and 47.5 T for $x = 0.5$, and $B_{\text{HF}} = 49.6$ and 48.0 T for $x = 1.0$ samples, respectively. The obtained IS parameters also confirmed the presence of only Fe^{3+} ions in these samples. Surprisingly, and as a consequence of the Mn addition, the doublet used to fit the MS spectrum of the undoped sample became a sextet with magnetic hyperfine fields of 45.0 T and 44.9 T for $x = 0.5$ and $x = 1.0$ samples, respectively. The Δ_{EQ} and IS parameters were found close to 0.09 mm/s and 0.39 mm/s, respectively, for both samples.

By analyzing the MS results it can be concluded that the Mn ions in BFO-BT s.s. are in the $3+$ valence state, whereas Mn^{2+} ions should contribute to form Fe^{2+} ions inside the samples following the equation $\text{Mn}^{3+} + \text{Fe}^{2+} \rightarrow \text{Fe}^{3+} + \text{Mn}^{2+}$. It is worth mentioning that the MS results showed only Fe^{3+} ions for all studied compositions. In fact, reported XPS studies [16,19] showed that small Mn amounts in BFO-based s.s. lead only to the formation of Mn^{3+} ions and, with Mn concentration increasing, the coexistence of Mn^{3+} and Mn^{2+} states emerges. Furthermore, the presence of Mn^{2+} ions tends to increase the concentration of oxygen vacancies and, consequently, tends to rise the leakage current [10]. This way, for practical applications the presence of only Mn^{3+} ions is highly desirable. Another interesting feature observed from the MS analysis is related to the transformation of the paramagnetic doublet of the undoped sample into a sextet in doped ones. These results strongly indicate a possible increase for the magnetic interactions in Mn doped BFO-BT s.s.

The magnetic hysteresis loops for Mn doped BFO-BT s.s. are shown in Fig. 4, while the inset shows the composition dependence of the remnant magnetization, M_r . The net magnetization of BFO-based s.s. is related to a canted antiferromagnetic order of Fe-O-Fe spin chains, although BFO does not show a net magnetization (or just a very small one) due to its cycloidal spin structure [4]. The BFO-BT undoped sample shows a linear magnetic field dependence of magnetization, practically without remnant magnetization in a typical antiferromagnetic-like behavior. In this way, it can be inferred that the cycloidal spin structure is still present in this sample. However, with Mn addition the BFO-BT s.s. show typical magnetic hysteresis loops with M_r ranging from 0.37 to 0.50 emu/g for $x = 0.3$ and $x = 1.0$, respectively. The coercive fields, H_C , also increase with Mn content increasing. It is worth noticing that these magnetic parameters are substantially higher than those found in literature for BFO-BT s.s. In fact, Liu et al. [10] obtained M_r of 0.1 and 0.15 emu/g for 0.3 and 0.5 wt% MnO_2 doped samples, while our results for these similar compositions are 0.37 and 0.4 emu/g, respectively. Other researchers [20] obtained even small values, as in the case of $0.9\text{BiFe}_{0.96}\text{Sc}_{0.04} - 0.1\text{BaTiO}_3$ s.s., where a maximum M_r of 0.49 emu/g for 7.0 wt% of MnO_2 was reported. For small quantities of MnO_2 , notably less than 2.0 wt%, they obtained a maximum M_r of approximately 0.05 emu/g.

This increase in magnetization has been attributed to the Jahn-Teller distortion effects occurring when Mn^{3+} ions occupy the B site of the perovskite structure [5,7,10]. In this approach the lattice around the Mn^{3+} ions is distorted, reducing the local symmetry and breaking the cycloidal spin structure with a consequent enhancement of M_r . Another explanation, suggested by Gehring et al. [21] is that the statistical distribution of Fe^{3+} or Ti^{4+} ions in the B sites, or the creation of lattice defects, is the responsible for the observation of a bulk (net) magnetization. Although these mechanisms may effectively contribute for the magnetization enhancement, they are in line with the same explanation found in the literature to justify the increase of magnetization with the increase of the BT content in BFO-BT s.s. [5,7]. However, the maximum M_r reported for BFO-BT s.s. is close

to 0.05 emu/g [5,22,20]. Therefore, it is seen that this magnetization increasing is not so significant as that observed for MnO₂ doped BFO-BT s.s. In this way, other mechanisms need to be considered to properly address this magnetization increase. In fact, from the MS analyses we found that the Fe ions, previously occupying paramagnetic sites in the undoped sample, became magnetically ordered in Mn doped BFO-BT s.s., definitively contributing for the magnetization increase. This change is probably due to the additional Mn³⁺ – O – Fe³⁺/Ti³⁺/Mn³⁺ superexchange interactions in Mn doped BFO-BT s.s., although further research is needed to completely characterize the intimate role of the Mn ions in this enhanced magnetism.

In summary, multiferroic Mn doped BFO-BT s.s. were prepared by high-energy ball milling and thermal treatments. All materials were crystalized in a perovskite structure with the coexistence of the *R3c* and *Cm* phases. Our studies also showed that the predominant valence state of the manganese ions are Mn⁺³, which is desired to obtain materials with high resistivity. The doped materials presented a significant improve in magnetization, showing a maximum remnant magnetization of 0.50 emu/g. To the best of our knowledge, this is the highest reported magnetization for BFO-BT s.s. Finally, the MS studies showed that this increase in magnetization can be related with an extra Fe³⁺ sextet that is only found in Mn doped samples.

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[1] N.A. Spaldin, m. Fiebig, Science 309 (2005) 391-392.

[2] M. Fiebig, J. Phys.D: Appl. Phys. 38 (2005) R123-R152.

[3] J.R. Teague, R. Gerson, W. James, Solid State Commun. 8(1970) 1073-1074.

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- [4] D. Lebeugle, D. Colson, A. Forget, M. Viret, A.M. Bataille, A. Gukasov Phys. Rev. Lett. 100 (2008) 227602.
- [5] R.A.M. Gotardo, L.F. Cótica, I.A. Santos, E. Botero, D. Garcia, J.A. Eiras, Scripta Mater. 61 (2009) 508-511.
- [6] L.F. Cótica, F.R. Estrada, V.F. Freitas, G.S. Dias, I.A. Santos, J.A. Eiras, D. Garcia, J. Appl. Phys. 111 (2012) 114105.
- [7] M.M. Kumar, A. Srinivas, S.V. Suryanarayana, J. Appl. Phys. 87 (2000) 855.
- [8] J.S. Kim, C. Cheon, C. Lee, P. Jang, J. Appl. Phys. 96 (2004) 468.
- [9] Y. Wei, X. Wang, J. Jia, X. Wang, Ceram. Int. 38 (2012) 3499-3502.
- [10] X. Liu, Z. Xu, S. Qu, X. Wei, J. Chen, Ceram. Int. 34 (2008) 797-801.
- [11] S.O. Leontsev, R.E. Eitel, J. Am. Ceram. Soc. 92 (2009) 2957-2961.
- [12] J. Chen, J. Cheng, J. Alloys and Compd. 589 (2014) 115-119.
- [13] R.A.M. Gotardo, D.S. Viana, M. Olzon-Dyonisio, S.D. Souza, D. Garcia, J.A. Eiras, M.F.S. Alves, L.F. Cótica, I.A. Santos, A.A. Coelho, J. Appl. Phys. 112 (2012) 104112.
- [14] J. Rodriguez-Carvajal, Physica B 192 (1993) 55-69.
- [15] Y. Guo, P. Xiao, R. Wen, Y. Wan, Q. Zheng, D. Shi K. Lam, M. Liu, D. Lin, J. Mater. Chem. C 3 (2015) 5811-5824.
- [16] T. Higuchi, W. Sakamoto, N. Itoh, T. Shimura, T. Hattori, T. Yogo, Appl. Phys. Express 1 (2008) 011502.
- [17] T. Park, G. Papaefthymiou, A. Viescas, Y. Lee, H. Zhou, S. Wong, Phys. Rev. B 82 (2010) 024431.
- [18] G.J. Long, F. Grandjean, Mössbauer Spectroscopy Applied to Magnetism and Materials Science Vol. 2 (Plenum, New York, 1996).
- [19] S. Unruan, S. Srilomasak, S. Priya, P. Jantaratana, S. Rujirawat, R. Yimnirun, Ceram. Int. 41 (2015) 4087-4092.

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- [20] M. Kumar, S. Shankar, R.K. Kotnala, O. Parkash, J. Alloy and Compd. 577 (2013) 222-227.
- [21] G.A. Gehring, Ferroelectrics 161 (1994) 275-285.
- [22] M.M. Kumar, S. Srinath, G.S. Kumar, S.V. Suryanarayana, J. Magn. Magn. Mater 188 (1998) 203-212.

Table and Table Caption

Table I. Rietveld refinement results for Mn doped 0.9BiFeO₃-0.1BaTiO₃ solid solutions.

Sample %Mn	Lattice parameter “a” - R3c (Å)	Lattice parameter “a” - Cm(Å)	Volume R3c (Å) ± 0.026	Ti/Fe/Mn position Z (Å)
0.0	5.577(4)	5.6828(2)	375.299	0.2199(4)
0.5	5.5912(5)	5.6860(3)	375.551	0.2230(2)
1.0	5.5915(4)	5.6867(6)	375.603	0.2242(6)

Figure Captions

Figure 1 –X-ray diffraction patterns for $0.9\text{BiFeO}_3 - 0.1\text{BaTiO}_3 - x \text{ wt.}\% \text{MnO}_2$ solid solutions. (a) $20 - 80^\circ$ and (b) $31 - 41^\circ$ regions, at room temperature.

Figure 2 – X-ray diffraction patterns and Rietveld refinement results for $0.9\text{BiFeO}_3 - 0.1\text{BaTiO}_3 - x \text{ wt.}\% \text{MnO}_2$ solid solutions, at room temperature.

Figure 3 – Mössbauer spectroscopic results (open circles) for $0.9\text{BiFeO}_3 - 0.1\text{BaTiO}_3 - x \text{ wt.}\% \text{MnO}_2$ solid solutions, at room temperature. The red line is the fitted spectrum and the green, brown and blue illustrations correspond to the fitted subspectra.

Figure 4 – Magnetic hysteresis loops for $0.9\text{BiFeO}_3 - 0.1\text{BaTiO}_3 - x \text{ wt.}\% \text{MnO}_2$ solid solutions, at room temperature. Inset: remnant magnetization as a function of the MnO_2 content.

Intensity (a.u.)

Transmission (%)