First detection of low field microwave absorption in the disordered multiferroic double perovskite BiFe$_{0.5}$Mn$_{0.5}$O$_3$

Brian Sibanda$^1$, Tebogo Sfiso Mahule$^1$, Davide Delmonte$^{2*}$, Andrea Sala$^3$, Edmondo Gilioli$^2$ and V V Srinivasu$^1$

$^1$ Department of Physics, University of South Africa, Johannesburg 1710, South Africa
$^2$ Institute of Materials for Electronics and Magnetism, IMEM-CNR, Parma, Italy
E-mail: davide.delmonte@imem.cnr.it

Keywords: low field microwave absorption, multiferroics, spontaneous magnetization reversal, electron spin resonance

Abstract

BiFe$_{0.5}$Mn$_{0.5}$O$_3$ (BFMO) is an intriguing magnetic double perovskite, only obtainable through high pressure-high temperature synthesis. It shows bulk multiferroic properties, namely the coexistence between a spin canted antiferromagnetic structure superimposed to an externally induced electric polarization at least from 77 K. In particular, the system is characterized by a significant weak ferromagnetic hysteresis loop and by a very rare phenomenon: the spontaneous magnetization reversal (MRV) versus temperature in the low field regime. To clarify the BFMO exotic magnetic phase in the low field regime, the Electron Spin Resonance (ESR) and the low field microwave absorption (LFMA) techniques were used, providing the first observation of LFMA in the bulk BFMO as an additional functionality of this material. A striking feature is that the hysteresis in LFMA signals vanishes above 45 K, while the bulk M–H loop hysteresis, measured in the same field range of LFMA, persists till room temperature. The temperature at which LFMA hysteresis vanishes qualitatively matches the position of the magnetic susceptibility’s second derivative peak, corresponding to the temperature at which the local second order mechanism responsible for MRV is maximum. The line shape of LFMA completely changes above 45 K and the ESR linewidth starts decreasing above this temperature, indicating the role of defect/disorder induced inhomogeneity. The temperature evolution of LFMA hysteresis and line shapes as a measure of the competition between Fe- and Mn-rich clusters suggests a sort of local frustration at the microscopic scale, responsible for the peculiar magnetization reversal of this system.

1. Introduction

Microwave absorption can be very sensitive to small magnetic fields in magnetic materials. A colossal magnetic field dependence of microwave loss, at very low fields (few hundred Oe), was firstly reported in the half-metal manganite system by Srinivasu et al [1, 2]. Later on, several groups have observed this low magnetic field dependent microwave absorption in different magnetic systems, such as, Co-based amorphous ribbons [3], glass-coated magnetic microwires [4, 5], ferrites [6], single and multilayer magnetic films [7–10], iron nanostructures [11], conducting polymers [12], iron nanoparticles embedded polyaniline nanofibers [13], dilute magnetic systems like Co-doped ZnO [14–16] and in the normal state of SmFeAsO$_{1-x}$F$_x$ iron-pnictides superconductors [17].

The low field microwave absorption (LFMA) technique has gained increasing attention in the last years both from the fundamental point of view and from the potential applied physics interest. Basically, this is a spin controlled phenomenon, where the sample is solely subjected to microwave magnetic field (not to the electric field). Specifically, since the microwave absorption is tuneable with very low applied magnetic fields, this leads to a field-controlled microwave absorber.
However, not every magnetic systems show the LFMA and the phenomenon itself is not fully understood, yet. It is therefore important to probe LFMA in novel magnetic systems to gather new insights. Besides, while most of the studied systems are magnetically well-ordered systems, the investigation of structurally and magnetically disordered or inhomogeneous systems is of fundamental interest. It is the case of BiFe0.5Mn0.5O3 (BFMO) [18–24], a multiferroic metastable double perovskite displaying bulk antiferromagnetism at about room temperature and an externally induced ferroelectric state up to liquid nitrogen boiling point. Thanks to these characteristics, this is a promising material for application in the fields of spintronics, double density data storage and electric and magnetic field mutual sensors.

Particularly, BFMO shows the peculiar feature of a spontaneous magnetization reversal (MRV) versus temperature in the low field regime, which is driven by the disorder at the B site of the double perovskite structure involving Fe and Mn. The well-studied bulk simple perovskite end-members (BiFeO3 and BiMnO3) [25–27] do not show this phenomenon, which is ruled out by the lack of cationic disorder in the structure. MRV was observed also in few other similar double perovskites [28, 29], but its origin is still debated. Based on the original hypothesis, the phenomenon is ascribed to the competition between Dzyaloshinskii-Moriya (DM) interaction, arising from a canted antiferromagnetic long-range ordering, and single ion anisotropy (SIA). A complementary approach describes the MRV in terms of a competition between magnetically independent subsystems, arising from disorder and inhomogeneity at the micro-scale.

We demonstrate that the latter applies well to BFMO, where the high pressure-high temperature (HP/PT) synthesis conditions induce intrinsic inhomogeneity on the perovskite B site, disorderly occupied by Fe/Mn magnetic ions. Such inhomogeneity creates, at the local scale and for low temperatures, weak competitions between clusters highly rich in Fe and highly rich in Mn. These interactions are then very sensitive to an external magnetic field, usually appearing only in the low field regime. This latter consideration makes BFMO suitable for the LFMA investigation.

2. Experimental

Bulk BFMO samples were synthesized in pure form (>95%) starting form binary oxides in HP/HT conditions at \( P = 6 \text{ GPa}, T = 1100 \degree \text{C} \) for 1.5 h, using a multi-anvil Walker-type press, as previously reported [18]. Magnetization thermal and field dependences were studied by MPMS-XL 5T SQuID Magnetometer by Quantum Design Corp.

The as-grown sample is characterized by a high degree of polycrystallinity, determined by the extreme thermodynamic synthesis conditions; consequently, crystallites’ size ranges from tens to hundred \( \mu \text{m} \). However, they intrinsically display a strong geminated nature, so that the single crystal unit is probably sub-micrometric. LFMA and ESR measurements were carried out using a Bruker ESR spectrometer, operating at 9.4 GHz. The DC field was spanned with a 100 KHz modulating field. The recorded LFMA and ESR signals are first derivatives of DC field. The sample was placed in a position of maximum microwave magnetic field \( (H_{\text{microwave}}) \) in the cavity of the spectrometer. Throughout the experiment \( H_{\text{microwave}} \) was perpendicular to the applied DC field. Temperature was varied using an Oxford instrument temperature controller and flow type cryostat. Low field magnetization hysteresis was measured using a Quantum Design PPMS system.

3. Results and discussion

It is reported in figure 1 the first observation of LFMA signal in a disordered BFMO polycrystalline sample in the very low field regime around 0 Oe. The LFMA phase, opposite to the regular ESR signal (with larger intensity at higher field), shows a minimum near zero. It is important to notice that LFMA usually occurs in small systems like micron, sub-micron powders and nano-scale thin films. For example, LFMA signal, first observed in micron size powders manganites, vanishes in the corresponding bulk form [1, 2]. Remarkably, it was possible to observe LFMA directly in the as-grown BFMO bulk pellet.

The evolution of LFMA as a function of temperature is shown in figure 2. The most important features are:

1. LFMA highlights hysteresis at 5 K and 20 K (figures 2(a) and (b), respectively). At 45 K (see figure 2(c)), the hysteresis collapses. From 45 K to 300 K (see figures 2(d)–(h)) LFMA presents a non-hysteretic behaviour: though the magnetization shows a substantial hysteresis as reported in figure 3. In comparison, a characteristic hysteresis data for LFMA and M-H loop, both collected at 70 K, are reported in figures 4(a) and (b).

This last observation depicts an intriguing scenario: LFMA hysteresis disappears at lower temperature, while a significant weak ferromagnetic hysteresis is retained in the M-H loop at higher temperatures.
Above 45 K, the LFMA shows different line shapes. It is well established that LFMA occurs when the sample is placed in $H_{\text{max}}$, maximum position in the cavity [1, 2], indicating that LFMA is originated by the spin system of the sample.

Figure 1. LFMA signal along with the ESR signal for the bulk BFMO sample measured at 300 K. Note the phase of LFMA is opposite to that of ESR signal.

Figure 2. Evolution of LFMA signal with different temperatures from 5 K to 300 K of BFMO pellet sample. Noteworthy, LFMA hysteresis vanishes at $T \geq 45$ K.

(2) Above 45 K, the LFMA shows different line shapes. It is well established that LFMA occurs when the sample is placed in $H_{\text{max}}$, maximum position in the cavity [1, 2], indicating that LFMA is originated by the spin system of the sample.
It is of fundamental importance to place BFMO sample in the cavity $H_{\text{inv}}$ maximum position to probe the spin system through LFMA.

LFMA hysteresis vanishes above 45 K and the line shape is different beyond 45 K, suggesting that LFMA is originated from two different spin subsystems in ranges of 5–45 K and 45–300 K, respectively.

Figure 3. Low field M-H hysteresis data for BFMO pellet collected at different temperature above 45 K.

Figure 4. (a) BFMO 70 K hysteresis data of LFMA. (b) M-H loops at the same temperature regime.
Different spin subsystems working in different ranges of temperature are well known in BFMO samples [18, 19]. For example, it was shown ([18], figure 10(a) herein), that the 5 K M-H loop clearly shows symmetric kinks. This was attributed to ‘soft’ and ‘hard’ magnetic components. Furthermore, spin canting is expected in this sample. Canted spin systems can be influenced by very low fields [30], which can aid the low field tunability or dependence of microwave absorption. However, there can be pinning defects, due to inherent disorder and inhomogeneity present in the sample, which can pin the canted spin domains and hinder their rotation with applied fields, leading to possible hysteresis in LFMA. Otherwise, the same hysteresis can arise from a weak interaction (as for instance a second order competition) acting in locking the canted spin rotation. This is what exactly happens in BFMO when the competition between different clusters (i.e., Fe-rich, and Mn-rich) is settled, precisely in the same thermal region in which the LFMA hysteretic behaviour is detected. This is supported also by linewidth analysis of ESR signal: it increased substantially around 45 K as the sample was cooled. Increase in ESR linewidths can be attributed to defects and inhomogeneities. Beyond 45 K, the linewidth decreased as shown in figure 5. Thus, thermal energy overcomes the pinning above 45 K. Both the ESR linewidths fall and the LFMA hysteresis collapse at 45 K. Above 45 K, the LFMA hysteresis vanishes and, moreover, the line shape changes completely, indicating that LFMA in the 45 to 300 K range presents different functional forms of dependence to the applied field. These findings confirm a lack of correlation and therefore a possible different origin for the two mentioned hysteretic behaviour. Nevertheless, the correlation can be found by comparing LFMA hysteresis with another phenomenon taking place in BFMO: the spontaneous MRV. It is interesting to notice that the LFMA hysteresis vanishes in the same thermal range in which the second derivative of the ZFC susceptibility reaches the maximum (figure 6, elaborated from ZFC collected at 100 Oe during the study reported in [19] and plotted as inset). This threshold represents the onset of a gradual decay of the ‘second-order’ interaction responsible for the MRV observed in BFMO.
LFMA drastically changes both hysteresis and line-shape around the same critical temperature where the second derivative of the ZFC magnetization shows the maximum. Therefore, LFMA seems to be able to probe the incoming interaction between the two independent magnetic subsystems responsible for MRV, thus sustaining the hypothesis proposed in the previous works [18, 19, 27, 28].

4. Conclusion

LFMA was reported for the first time in the disordered and exotic bulk double perovksite BFMO, obtained by HP/HT synthesis. This is a new functionality of this intriguing material. This system is known to be multiferroic at least up to the liquid nitrogen boiling point and to display spontaneous reversal magnetization versus temperature arising from the magnetic a very weak competition between different spin subsystems characterized weak ferromagnetic interactions determined by the canted antiferromagnetic structure. The LFMA hysteresis properties are totally different from that of magnetization hysteresis. LFMA hysteresis evidence two regimes: (1) below 45 K, LFMA has a measurable hysteresis; while (2), from 45 K, hysteresis collapses and completely vanishes up to 300 K. Moreover, the line shape of LFMA changes completely in these two temperature ranges. This is indicative of two different functional dependence of LFMA from applied low field and the related spin subsystems. The behaviour is proved with an ESR linewidth observation that started a decreasing trend above 45 K.

On the fundamental side, LFMA data clearly establish the existence of two spin subsystems. Hysteresis in the LFMA overlaps to the magnetic regime of BFMO in which the negative response under positive field (magnetization reversal) is stabilized, thus in the region in which the strong competition of the different subsystems is maximum. However, the magnetization and LFMA data depends on these two competing subsystems differently. The question why LFMA and magnetization responses depend on the two spin subsystems, opens to theoretical debate and to further experimental investigations.

On the applied science aspect, the fact that LFMA occurs in the bulk form of materials, is a new and important feature by itself, as all the previous LFMA studies were reported on 'small' systems (e.g. micron size powders, thin films, and nano-systems). Indeed, first observation of low field tuneable microwave absorption in bulk materials means that it is possible to obtain such a property without going through complex processes usually needed to obtain low dimensional or nanoscaled systems.

Acknowledgments

The work is carried out in the framework of Italy South Africa bilateral mobility Research Project (ISARP) N° ZA18MO03 for the years 2018–2020 (extended to 2021 due to Covid-19 pandemic) funded by the Italian Ministry of Foreign and Communitarian Affairs and the South Africa’s National Research Foundation (NRF).

Data availability statement

The data that support the findings of this study are available upon reasonable request from the authors.

ORCID iDs

Davide Delmonte @ https://orcid.org/0000-0001-5367-527X
Andrea Sala @ https://orcid.org/0000-0001-7265-9187

References

[1] Srinivasu V V, Lofland S E and Bhagat S M 1998 J. Appl. Phys. 83 2866
[2] Srinivasu V V, Lofland S E, Bhagat S M, Ghosh K and Tung S D 1999 J. Appl. Phys. 86 1067
[3] Montiel H, Alvarez G, Betancourt I, Zamorano R and Valenzuela R 2005 Appl. Phys. Lett. 86 072503
[4] Chiriac H, Colesnicu C N and Ovari T A 2000 J. Magn. Magn. Mater. 215–216 607
[5] Montiel H, Alvarez G, Gutierrez M P, Zamorano R and Valenzuela R 2006 IEEE T. Magn. 42 3380
[6] Montiel H, Alvarez G, Gutierrez M P, Zamorano R and Valenzuela R 2004 J. Alloy. Compd. 369 141
[7] Dubowik J and Stobięcki F 2002 Czech. J. Phys. 52 227
[8] Gavi H, Ngom B D, Beye A C, Srydum A M, Srinivasu V V, Chaker M and Manyala N 2012 J. Magn. Magn. Mater. 324 1172
[9] Lee J, Kim J and Kim K H 2014 Phys. Status Solidi A 211 1900
[10] Kim J, Kim J and Kim K H 2014 Appl. Phys. Lett. 103 143508
[11] Felix J F, Figueriredo L C, Mendes J B S, Morias P C and De Araujo C I L 2015 J. Magn. Magn. Mater. 395 130
[12] Khairullin I L, Khabbiullaev P K, Sokolov V Y and Zakhidov A A 1999 Turk. J. Phys. 23 1107 (https://journals.tubitak.gov.tr/physics/abstract.htm?id=3676)
[13] Bhaumik M, Maity A, Mahule T S and Srinivasu V V 2019 Synthetic Met. 249 63
[14] Mahule T S, Srinivasu V V and Das J 2016 Solid State Commun. 243 60
[15] Mahule T S, Das J, Sahu D R and Srinivasu V V 2018 Acta Phys. Pol. A 134 326
[16] Onyancha R B, Shimoyama J, Das J, Ogino H, Aigbe U O and Srinivasu V V 2020 Solid State Commun. 307 113800
[17] Mahule T S, Das J and Srinivasu V V 2019 Appl. Phys. A 125 231
[18] Delmonte D et al 2013 Phys. Rev. B 88 014431
[19] Delmonte D, Mezzadri F, Pernechele C, Gilioli E, Celestani G, Cabassi R, Bolzoni F, Spina G, Lantieri M and Solzi M 2015 J. Phys. Condens. Matter 27 286002
[20] Delmonte D, Mezzadri F, Gilioli E, Solzi M, Celestani G, Bolzoni F and Cabassi R 2016 Inorg. Chem. 55 6308
[21] Mandal P et al 2010 Phys. Rev. B 82 100416R
[22] Belik A A, Abakumov A M, Tsirlin A A, Hadermann J, Kim J, Van Tendeloo G and Takayama-Muromachi E 2011 Chem. Mater. 23 4505
[23] Dasari N, Mandal P, Sundaresan A and Vidhyadhara N S 2012 Europhys. Lett. 99 17008
[24] Belik A A 2013 Inorg. Chem. 52 2015–21
[25] Sriari N V, Vinayakumar K B and Nagaraja K K 2020 Coatings 10 1221
[26] Sugawara F, Jiida S, Syono Y and Akimoto S 1968 J. Phys. Soc. Jpn. 25 1553–8
[27] Ederer C and Spaldin N A 2005 Phys. Rev. B 71 060401(R)
[28] Ren Y, Palstra T T M, Khomskii D I, Pellegrin E, Nugroho A A, Menovsky A A and Sawatzky G A 1998 Nature 396 441
[29] Belik A A 2015 Sci. Technol. Adv. Mater. 16 026003
[30] Hao L et al 2018 Nat. Phys. 14 806