Polymer-based Magnetoelectric Materials: *To be* or *not to be*

Pedro Martins[1] *and Senentxu Lanceros-Méndez*[2,3]*,*

1. Centro/Departamento de Física, Universidade do Minho, Braga 4710-057, Portugal
2. BCMaterials, BCMaterials, Basque Center for Materials, Applications and Nanostructures, UPV/EHU Science Park, 48940 Leioa, Spain
3. IKERBASQUE, Basque Foundation for Science, 48013 Bilbao, Spain

Nearly twenty years ago, the 'polymer-based magnetoelectrics' concept changed thinking in multiferroic magnetoelectric materials research, resulting in a generation of new high-performance materials and an increased focus on controlling structure, flexibility and electric output, as well as implementation into proof of concept applications.

"*To be, or not to be*" is the opening phrase of a soliloquy speech by Prince Hamlet in the so-called "nunnery scene" of William Shakespeare's world famous play Hamlet. Act III, Scene I. There are many "interpretations" of such speech, nevertheless the most accepted ones are related to viable solutions to some problems, our attitude towards a fracturing event, if we should risk or remain passive and if the reward deserves the sacrifices. Hamlet was considering the difficulties and pondering a state of being versus a state of not being – being alive and being dead. The play was written in 1599-1601, at the same time that William Gilbert suggested that magnetism was "*the soul of the Earth*" (1600) and long before Gowen Knight produced the first artificial magnets for scientific research and navigation (1740); Hans Christian Oersted proved experimentally the physical relationship between electricity and magnetism (1820); the enunciation of the possibility of magnetoelectric (ME) effect on moving crystals by Pierre Curie (1894); the report of ME in composites of piezoelectric and piezomagnetic phases (1994); the renaissance of magnetoelectric effect (2005) and the publication of the first book on polymer-based ME materials (PBMM) (2017), summarizing the main achievements in the field. PBMM have already demonstrated strong potential for implementation into device applications, nevertheless it is still desirable materials to show higher performance, simpler processability and reliability.

Some years ago PBMM emerged as a solution to solve the main problems associated to single-phase multiferroics (low ME response at low temperatures) and ceramic-based (fragility, high dielectric losses and complicated processing procedures) ME materials[1-3]. Rapidly, they showed potential applicability in areas such as sensors, actuators, biomedicine and tissue engineering, energy harvesting (EH), antennas and memories[2,4].

Figure 1a shows that the first device applications to attract the interest of scientific community was area of sensors. This fact can explain the high number of papers published (1246) in less than 10 years in this specific area.

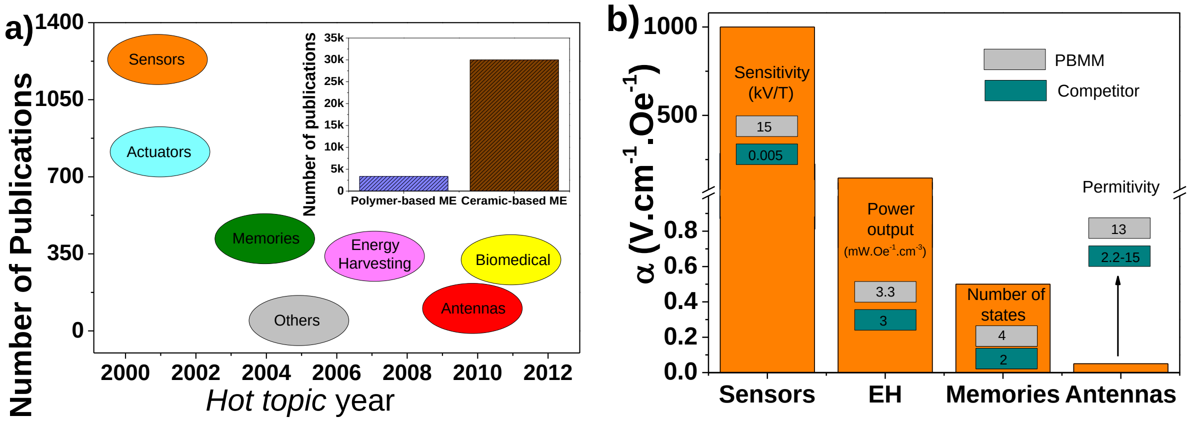
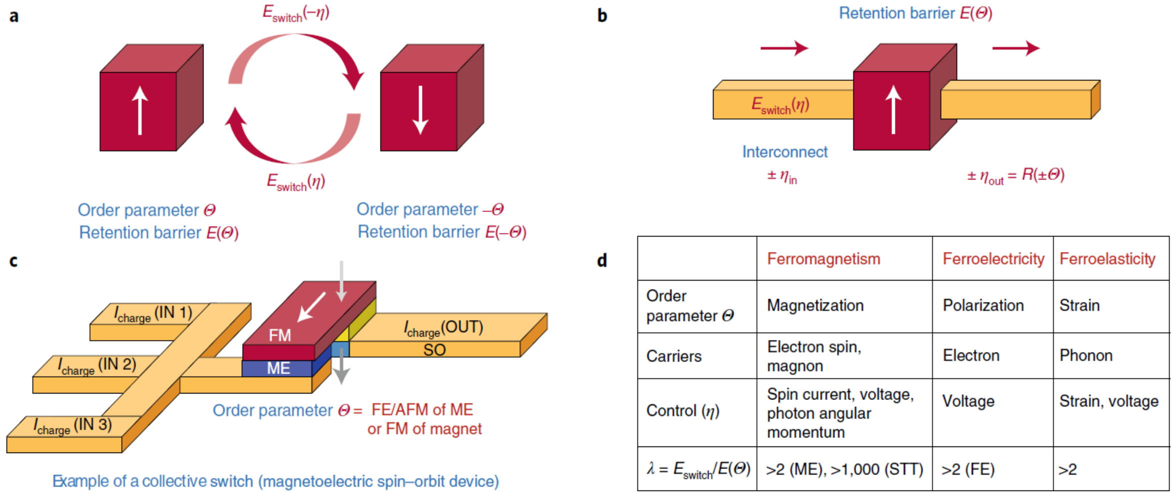


Figure 1 | a, Number of publications (SCOPUS database) related with applications of polymer-based ME materials and the year in which the application has become a *hot topic* (paper with more than 100 citations). The inset shows the difference between the total number of papers published on polymer-based ME materials and ceramic-based ME materials. **b,** ME coefficient (α) reported for each device application and corresponding figure of merit (FOM) compared with the "technological competitor", a device for the same application based on a different technology.

In an intermediate place appear the activity of ME actuators (817 publications), exploring the wireless control of the electrical and/or mechanical response of a mechanism or system. With less than 400 publications each, appear the contributions in the areas of memories, energy harvesters, antennas and the most recent applications related to biomedicine and tissue engineering.

Contrary to what it could be expected, the highest ME response reported in the literature for a PBMM device was not for energy harvesting (146 $Vcm^{-1}Oe^{-1}$) but for magnetic sensing ($1kVcm^{-1}Oe^{-1}$). Polymer-based ME materials developed for data memories exhibit an intermediate ME coupling, while antennas show the lowest ME response ($50mV.cm^{-1}Oe^{-1}$).

Particularly interesting is the analysis of the figures of merit of the different polymer-based ME devices, when compared to a competitive technology well-stablished in the market. Thus, PBM magnetic field sensors exhibit a 15 $kV.T^{-1}$ sensitivity (0.005 $kV.T^{-1}$ for Hall sensors)[5], PBM harvesters reveal a power output of 3.3 $mW.Oe^{-1}.cm^{-3}$ (3 $mW.Oe^{-1}.cm^{-3}$ for helical core magnetic harvester)[6,7], PBM show 4 memory states (2 on traditional magnetic recording devices)[8] and the relative permittivity is 13 in PBM antennas (2.2-15 for wide bandwidth antennas)[9]. Of course, other technologies could have been indicated for each application, the relevant presented ones indicating nevertheless the suitability of the state of the art of polymer-based ME materials response, for a wide range of applications. All these interesting indicators show that the Achilles' heel regarding the implementation of PBMM in device applications is no longer related to the ME output of the polymer-based material. Thus, the main issues that should be addressed in order to “bridge the gap” to actual applications are related to processability, device integration and reliability[10]. In the case of sensing, the reduction of equivalent magnetic noise remains a problem that should be addressed[11] while in the case of PBM memories and with the continuing demand for ultra-high-density data storage applications, it is becoming increasingly important to scale down the dimension of multiferroic structures to nanoscale arrays such as nanodot arrays[12,13], the nanostructuring of both polymer and magnetic phases will play a key role in this challenge. PBM memories can also provide new variables for computing, interconnects and memory, relying on intrinsic parameters such as magnetization, strain and polarization, revealing collective switching, non-volatility and strong thresholding behaviour. This concept of collective switching has been recently reported on[14] and should be extended to PBMM witch a magnetic/multiferroic (MF) state by allowing a successful switching on a volume of 1,000 nm^3 with a stability of 100 kBT.



	Ferromagnetism	Ferroelectricity	Ferroelasticity
Order parameter Θ	Magnetization	Polarization	Strain
Carriers	Electron spin, magnon	Electron	Phonon
Control (η)	Spin current, voltage, photon angular momentum	Voltage	Strain, voltage
$\lambda = E_{switch}/E(\Theta)$	>2 (ME), >1,000 (STT)	>2 (FE)	>2

Figure 2 | Definition of a collective switch. a, Collective state switch for using the materials' order parameter. The two states are given by values of ± Θ. **b,** Interconnect providing an input to and output when the switch carries a signal ± η. The state of the device is detected and transduced to the output ± ηout = R(± Θ). **c,** Example of a collective switch, a magnetoelectric spin–orbit logic device where the order parameters are ferroelectric/antiferromagnetic (FE/ AFM) of the magnetoelectric (ME), and the read-out is via spin–charge conversion**. d,** Potential order parameters, carriers and control variables are shown. The figure of merit λ = Esw/Δ E(Θ) allows identification of potential for an efficient logic device/switch. STT, spin-transfer torque**.**

With respect to energy harvesting it is important to decrease the impedance, increase the current and enhance magnet and coil qualities[15]. This is the only application in which the optimization of the ME response can still be essential for its successful implementation, once it is directly related with its efficiency. PBMM for antenna device applications need further and deeper studies that report their radiation pattern, power density, directivity, efficiency, gain and impedance, as has already reported for ceramic-based ME materials[16]. This is, in fact, one of the application with larger growth possibilities in the next years due to the high demand from end-use industries, attributed to the use of antennas for satellite communication, Wi-Fi routers and radar communications[17,18].

Mechanisms driving multiferroicity are far from being fully explored. Namely, there can be many ways to obtain a magnetic order to control a non-stabilized ferroelectric state. Some of them may lead to inherently improved ordering temperatures and polarization compared with those of the current spin-driven ferroelectrics[10]. Nevertheless, a PBMM device in which the magnetization is controlled by an applied electric field, if possible at low voltages, close to room temperature and with ultrafast switching, remains unreported[10].

The time of simple material combination, marginal increase of the ME response, and conventional lab approaches heads towards the end. The challenges to be tackle are at the level of control electronics, integration into devices, miniaturization to the nanoscale level, multifunctional approaches and device's FOM (better performance, new functionalities, cheaper materials).

It is also time to solve the two main problems in this interesting research field: i) to improve integration for the in the need of using two magnetic fields (one AC and one DC) to obtain the ME response and; ii) to obtain higher ME response on PBM nanocomposites (in the same order of laminates). The first one can be solved with the incorporation of permanent magnets (DC field) or miniaturized AC coils in the ME device, thus making the device work in more realistic conditions. The second one requires a more disruptive approach such as the use of new phenomena to induce the ME coupling. The use of magnetic-ionic materials seems a good approach that has not yet been sufficiently explored. In this methodology the relation between the magnetic and the electric order would not be mediated by the stress but by the movement of ions within the ferroelectric polymer.

When the device performances of PBMM materials would be reported in detail, manufacturing processes and device integration will remain the final step to commercial applications. Being polymer based materials, printing technologies may be used in PBMM to promote reduced cost of assembly, easy integration into devices and the possibility to obtain multifunctional materials over flexible and large areas[19]. The lead-free PBMM approach will allow the fabrication of products that are ecofriendly and safe[20,21].

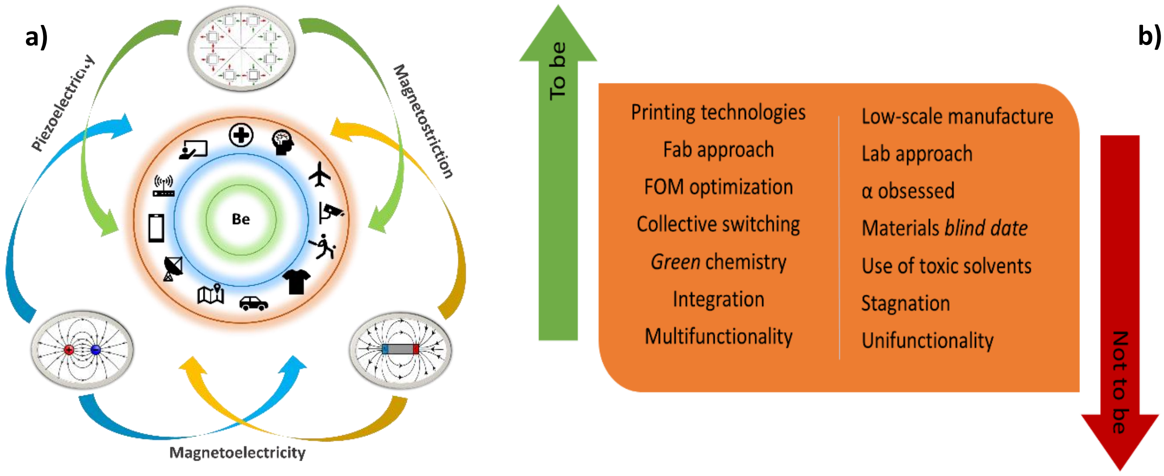


Figure 3 | PBMM *to be* or *not to be*. a, Potential applications of PBMM. **b,** Schematic representation of the main challenges of PBMM materials.

Another key issue lies in in the diversification of the materials used in ME composites. 90% of the works are related to polyvinylidene fluoride (PVDF) and its copolymers[1,22]. Polymers such as aromatic polyimides[23], cellulose[21] and poly(lactic acid) (PLLA)[24] can open new application possibilities, namely on high-temperature, biocompatible and biodegradable devices, respectively.

Finally, and although there is still room for more fundamental research, the progress in PBMM can open other variety of applications (Figure 3a) such as low-voltage radio frequency MEMS switches and resonators, film-type speakers, flexible displays, soft haptic devices, actuators for millimeter-scale robotics, droplet ejectors and medical imaging transducers[20]. In particular, novel aspects of electric field control of magnetic domain switching are highly appealing. However, there are still some further studies needed to achieve breakthroughs and to push this area to real applications[12,25]. Other innovative approaches still need to be optimized such as wearable PBMM, neuro PBMM nanotransducers and energy harvesters for wireless sensors and structural health monitoring.

To be or *not to be* is no longer an existential question in this area, it represents a bifurcation in today's research in this field. The traditional and conservative way which will lead to expected results and consequent stagnation, and another more challenging route which will certainly lead to a deeper understanding of the ME coupling in polymer based materials and to the successful implementation of PBMM on nowadays and future applications (Figure 3b).

William Shakespeare, also in Hamlet (Act 2, Scene 2), wrote *“that there is nothing either good or bad, but thinking makes it so”* so … let´s think and act in a right way to make polymer-based ME materials a key enabling technology.

References

(1) Martins, P.; Lanceros-Mendez, S. In *Magnetoelectric Polymer-Based Composites*; Wiley-VCH Verlag GmbH & Co. KGaA: 2017, p 255.

(2) Martins, P.; Lanceros-Méndez, S. *Advanced Functional Materials* **2013**, *23*, 3371.

(3) Zhao, W.; Liu, Z.; Wei, P.; Zhang, Q.; Zhu, W.; Su, X.; Tang, X.; Yang, J.; Liu, Y.; Shi, J.; Chao, Y.; Lin, S.; Pei, Y. *Nature Nanotechnology* **2017**, *12*, 55.

(4) Kosub, T.; Kopte, M.; Hühne, R.; Appel, P.; Shields, B.; Maletinsky, P.; Hübner, R.; Liedke, M. O.; Fassbender, J.; Schmidt, O. G.; Makarov, D. *Nature Communications* **2017**, *8*.

(5) Reis, S.; Castro, N.; Silva, M. P.; Correia, V.; Rocha, J. G.; Martins, P.; Lanceros-Mendez, S. *IEEE Transactions on Industrial Electronics* **2017**, *64*, 4828.

(6) Lasheras, A.; Gutiérrez, J.; Reis, S.; Sousa, D.; Silva, M.; Martins, P.; Lanceros-Mendez, S.; Barandiarán, J. M.; Shishkin, D. A.; Potapov, A. P. *Smart Materials and Structures* **2015**, *24*.

(7) Yuan, S.; Huang, Y.; Zhou, J.; Xu, Q.; Song, C.; Yuan, G. *IEEE Transactions on Power Electronics* **2017**, *32*, 5365.

(8) Lu, P.; Shang, D.; Shen, J.; Chai, Y.; Yang, C.; Zhai, K.; Cong, J.; Shen, S.; Sun, Y. *Applied Physics Letters* **2016**, *109*.

(9) Raj, P. M.; Sharma, H.; Reddy, G. P.; Altunyurt, N.; Swaminathan, M.; Tummala, R.; Nair, V. *Journal of Electronic Materials* **2014**, *43*, 1097.

(10) Fiebig, M.; Lottermoser, T.; Meier, D.; Trassin, M. *Nature Reviews Materials* **2016**, *1*.

(11) Wang, Y.; Li, J.; Viehland, D. *Materials Today* **2014**, *17*, 269.

(12) Chen, D.; Gao, X.; Liu, J. M. *MRS Communications* **2016**, *6*, 330.

(13) Tokura, Y.; Kawasaki, M.; Nagaosa, N. *Nature Physics* **2017**, *13*, 1056.

(14) Manipatruni, S.; Nikonov, D. E.; Young, I. A. *Nature Physics* **2018**, *14*, 338.

(15) Narita, F.; Fox, M. *Advanced Engineering Materials* **2017**.

(16) Nan, T.; Lin, H.; Gao, Y.; Matyushov, A.; Yu, G.; Chen, H.; Sun, N.; Wei, S.; Wang, Z.; Li, M.; Wang, X.; Belkessam, A.; Guo, R.; Chen, B.; Zhou, J.; Qian, Z.; Hui, Y.; Rinaldi, M.; McConney, M. E.; Howe, B. M.; Hu, Z.; Jones, J. G.; Brown, G. J.; Sun, N. X. *Nature Communications* **2017**, *8*.

(17) market, M. a. *Metamaterial Market by Material Type (Electromagnetic, Terahertz, Photonic, Tunable, and FSS), Application (Communication Antenna, Windscreen, Solar Panel, Sensing, Display, and Medical Imaging),*, 2017.

(18) Research, M. I. M. *Global Antenna Market - Segmented by Type, End-user Industry, Application, and Region - Growth, Trends and Forecast (2018 - 2023)*, 2018.

(19) Oliveira, J.; Correia, V.; Castro, H.; Martins, P.; Lanceros-Mendez, S. *Additive Manufacturing* **2018**, *21*, 269.

(20) Khan, A.; Abas, Z.; Soo Kim, H.; Oh, I. K. *Smart Materials and Structures* **2016**, *25*.

(21) Zong, Y.; Zheng, T.; Martins, P.; Lanceros-Mendez, S.; Yue, Z.; Higgins, M. J. *Nature Communications* **2017**, *8*.

(22) Martins, P.; Lopes, A. C.; Lanceros-Mendez, S. *Progress in Polymer Science* **2014**, *39*, 683.

(23) Maceiras, A.; Martins, P.; Gonc¸alves, R.; Botelho, G.; Venkata Ramana, E.; Mendiratta, S. K.; San Sebastián, M.; Vilas, J. L.; Lanceros-Mendez, S.; León, L. M. *European Polymer Journal* **2015**, *64*, 224.

(24) Barbosa, J.; Correia, D. M.; Gonçalves, R.; Ribeiro, C.; Botelho, G.; Martins, P.; Lanceros-Mendez, S. *Advanced Healthcare Materials* **2016**, *5*, 3027.

(25) Carvell, J.; Cheng, R.; Dowben, P. A.; Yang, Q. *Applied Physics Letters* **2013**, *103*.

ACKNOWLEDGMENTS

The authors thank the FCT - Fundação para a Ciência e Tecnologia - for financial support under framework of the Strategic Funding UID/FIS/04650/2013 and project PTDC/EEI-SII/5582/2014. Funds provided by FCT in the framework of EuroNanoMed 2016 call, Project LungChek ENMed/0049/2016 are also gratefully acknowledged as well as the FCT grant

SFRH/BPD/96227/2013 (PM). The authors also acknowledge funding by the Spanish Ministry of Economy and Competitiveness (MINECO) through the project MAT2016-76039-C4-3-R (AEI/FEDER, UE) and from the Basque Government Industry Department under the ELKARTEK and HAZITEK program.