Thomas Lottermoser and Dennis Meier*

A short history of multiferroics

Abstract: The realization that materials with coexisting magnetic and ferroelectric order open up efficient ways to control magnetism by electric fields unites scientists from different communities in the effort to explore the phenomenon of multiferroics. Following a tremendous development, the field has now gained some maturity. In this article, we give a succinct review of the history of this exciting class of materials and its evolution from "ferroelectromagnets" to "multiferroics" and beyond.

Keywords: multiferroic, ferroelectric, ferromagnetic, magnetoelectric

1 From ferroelectromagnets to multiferroics

Hans Schmid coined the term *multiferroic* in 1993 in Ascona [1], complementing the earlier classification of *ferroic* materials by Aizu [2] . He defined multiferroics as materials that unite two or more primary ferroic states (ferroelasticity, ferroelectricity, ferromagnetism and ferrotoroidicity [1, 3]) in the same phase (Figure 1). A subset of these multiferroic materials is also magnetoelectric, i.e. these materials display a coupling between their electric and magnetic properties [5]. This coupling is the main reason for the world-wide interest in multiferroics, as it enables the control of magnetic order by electric fields and vice versa. While the term *magnetoelectric* originally referred to a linear coupling between electric (magnetic) field and magnetization (electric polarization), we nowadays include all types of coupling phenomena that occur between charge and spin degrees of freedom when talking about magnetoelectric multiferroics [6]. Furthermore, going beyond just primary ferroic states, the initial concept of coexisting orders has been expanded, now also including, e.g. antiferromagnetism and multi-phase materials like laminates, solid solutions, and layered (thin film) architectures [7–12]. In this work, we will use this modern interpretation when referring to multiferroics.

Although the term multiferroics appeared in literature only around the year 2000, it is important to note that the hunt for a strong coupling of magnetic and electric degrees of freedom as basis of novel voltage-controlled low-power magnetic devices

***Corresponding author: Dennis Meier,** Department of Materials Science and Engineering, NTNU Norwegian University of Science and Technology, Sem Sælandsvei 12, Trondheim 7034, Norway, E-mail: dennis.meier@ntnu.no
Thomas Lottermoser, Department of Materials, ETH Zurich, Vladimir-Prelog-Weg 4, Zurich, ZH 8093, Switzerland, E-mail: thomas.lottermoser@mat.ethz.ch

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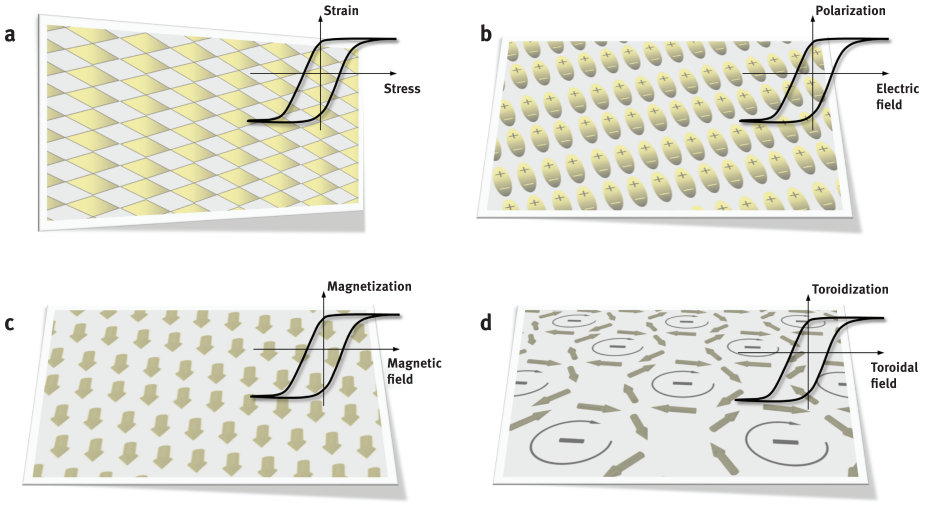

Figure 1: Primary ferroic order. Four types of ferroic order are classified as primary ferroic properties, namely ferroelasticity (a), ferroelectricity (b), ferromagnetism (c), and ferrotoroidicity (d) [1]. (a) Ferroelastics exhibit spontaneous strain, σ, which can be switched between equally stable states by application of stress. (b) Ferroelectrics develop a spontaneous electric polarisation, P, which switches under application of an electric field. (c) In ferromagnets, the spontaneous alignment of spins results in a macroscopic magnetic moment, M. This spontaneous magnetization can be switched by a magnetic field. (d) Ferrotoroidicity is discussed as fourth type of primary ferroic order [3, 4]. For example, ferro-toroidics may exhibit a vortex-like alignment of spins with a toroidization (T). The toroidal field required to switch the order is of the form E x H, where E and H are the electric and magnetic field, respectively. In the classical definition, a multiferroic material simultaneously shows two or more of these ferroic properties in the same phase. Nowadays, however, the term is used in a much broader context as discussed in the main text. Insets: A key characteristic of any primary ferroic order is its hysteretic response to the conjugated field (e.g. $P \leftrightarrow E$, $M \leftrightarrow H$). In the ideal multiferroic, P and M are coupled so that the magnetic order, M, can be switched by an electric field and the electric order, P, by a magnetic field H.

began already decades earlier [13]. The research on new types of electric and magnetic long-range order really flourished during the first half of the 20th century; two outstanding events that date back to this time are the experimental discovery of ferroelectricity by Valasek [14] and Néel's seminal work on antiferromagnetism [15]. The theoretical description of ferroelectricity and antiferromagnetism progressed rapidly, but measurements were challenging. Thus, from an experimental point of view, these physical phenomena were still rather new in the 1950s when first efforts to combine magnetic and ferroelectric order were pursued in the former Soviet Union. Smolenskii and Ioffe suggested to introduce magnetic ions into ferroelectric perovskites and create magnetic long-range order while retaining the ferroelectric state [16]. Their research led to the successful synthesis of single-crystals like $Pb(Fe_{0.5}Nb_{0.5})O_3$ and polycrystalline solid-solutions like $(1–x)Pb(Fe_{0.66}W_{0.33})O_3–xPb(Mg_{0.5}W_{0.5})O_3$, representing first

multiferroics that were designed on purpose [17, 18]. Smolenskii and Ioffe referred to these systems as *ferroelectromagnets* (orginally: *seignettomagnets*).

Interestingly, two of the most intensely investigated present-day multiferroics, that is, $BiFeO_3$ and the hexagonal (h-) manganites ($RMnO_3$, R = Sc, Y, In, Dy-Lu), have already been identified in the early 1960s [19–22]. The celebrity of the first multiferroics era, however, were the boracites. In 1966, Asher *et al.* observed a colossal linear magnetoelectric effect in $Ni_3B_7O_{13}I$ that allowed for hysteretic switching of a multiferroic state by either electric or magnetic fields [23]. Such experimental findings were complemented by the development of a theoretical framework, predictions about emergent magnetoelectric phenomena, and the proposition of technological applications [24]. The latter were remarkably similar to modern multiferroic-based device paradigms. Moreover, classical theory tools, such as representation analysis and Landau theory, still play a key role for the description of multiferroics. Around 1970 Aizu developed a unifying classification of ferroics [2, 25]. This contributed significantly to the modern understanding of (multi-)ferroics and to Schmid's important definition [1].

Following the peak in research activities in the 1960s, the first multiferroics era petered out about a decade later. By that time, circa 50 multiferroic systems were known [26], none of which exhibited technologically feasible properties. This may explain why researchers eventually lost interest and moved on to other material classes. Of course, the research on multiferroics never stopped completely. One seminal discovery was made in 1978 by Newnham and coworkers, who reported that a spin spiral in Cr_2BeO_4 breaks spatial inversion symmetry and thereby induces a spontaneous electric polarization [27]. On just four pages the authors foreshadow much of the fascinating physics of magnetically driven (improper) ferroelectricity that should be recognized much later as key source for multiferroics with strong magnetoelectric interactions. Five years later, in 1983, Bar'yakhtar *et al.* presented a phenomenological model, elaborating how magnetic order can break inversion symmetry and, hence, induce an electric polarization [28].

The ball was set rolling again when Hans Schmid organized a conference on Magnetoelectric Interaction Phenomena in Crystals (MEIPIC-2) in 1993. The meeting and its fascinating proceedings identified and interrelated many of the phenomena, systems and theories surrounding the magnetoelectric effect [29]. Aspects crucial to the resurgence of multiferroics, such as techniques for imaging multiferroic domains and their interactions, new types of ferroic order and future multiferroic key materials, can all be traced back to MEIPIC-2.

In 2000, Spaldin (then Hill) revisited the original idea of Ioffe and Smolenskii and elaborated why in classical perovskites, displacive ferroelectricity and magnetic order are working against each other [30]. This work and a session at the 2000 March Meeting of the American Physical Society reached out to a broad audience and further prepared the stage for the second era of multiferroics. Encouraged by the knowledge of why previous attempts to expand the pool of multiferroics had

stagnated and the interim progress in materials synthesis and characterization, researchers accepted the challenge and resumed the hunt for novel multiferroics of technological value.

First highlights were the discoveries of pronounced magnetoelectric interactions in h-$YMnO_3$ [31, 32], orthorhombic $TbMnO_3$ [33], and $TbMn_2O_5$ [34]. In the latter two materials, the interaction originates from non-centrosymmetric spin textures inducing a magnetically controllable electric polarization, analogous to the case of Cr_2BeO_4. In contrast to the earlier work on Cr_2BeO_4, however, the new findings succeeded in triggering world-wide attention, leading to concerted efforts in different communities, bridging materials science, condensed matter physics, and materials theory. It was this joint effort of a new generation of researchers which promoted multiferroics research to new realms (for a detailed review on the early history of multiferroics, we refer the reader to the extended work in, e.g. [13, 26, 35]).

2 The second era of multiferroics

Just as 40 years earlier, the new quest for multiferroics with strongly interacting magnetic and electric order had a strong focus on ferroelectrics. This time, however, the scope was to find novel types of polar states that permit the emergence of coexisting magnetic order – an approach that went far beyond a mere revival of existing concepts. Theoretical and experimental tools had advanced tremendously compared to the first era of multiferroics. It was now possible to understand multiferroicity at the atomic scale and, importantly, design new systems with unprecedented precision and complexity. This was essential for accomplishing the shift away from standard displacive ferroelectrics and towards materials where, e.g. the electric polarization is induced by the spin system rather than counteracting the magnetic ordering [36–38]. Foreshadowing such so-called improper ferroelectrics [39], Levanyuk and Sannikov already mentioned in 1974 that “a complicated change in the crystal or magnetic structure” can induce an electric polarization [40]. Now, scientists began to elaborate such “complicated change” in minute detail and improper ferroelectricity became a key component in the hunt for novel single-phase multiferroics with pronounced magnetoelectric coupling.

From an academic point of view, one of the main achievements associated with the second era of multiferroics was the development of a comprehensive framework that allowed to classify all known materials with respect to the mechanism that drives multiferroicity. Nowadays, we distinguish four classes of multiferroics with ferroelectricity driven by electronic lone pairs, geometry, charge ordering, and magnetism as summarized in Figure 2 [12].

The so-called **lone-pair mechanism** is based on the violation of inversion symmetry by valence electrons (Figure 2(a)). This mechanism is responsible for the room-temperature ferroelectricity in $BiFeO_3$ ($T_C = 1103\,K$) [46]. Here, two of the Bi^{3+}

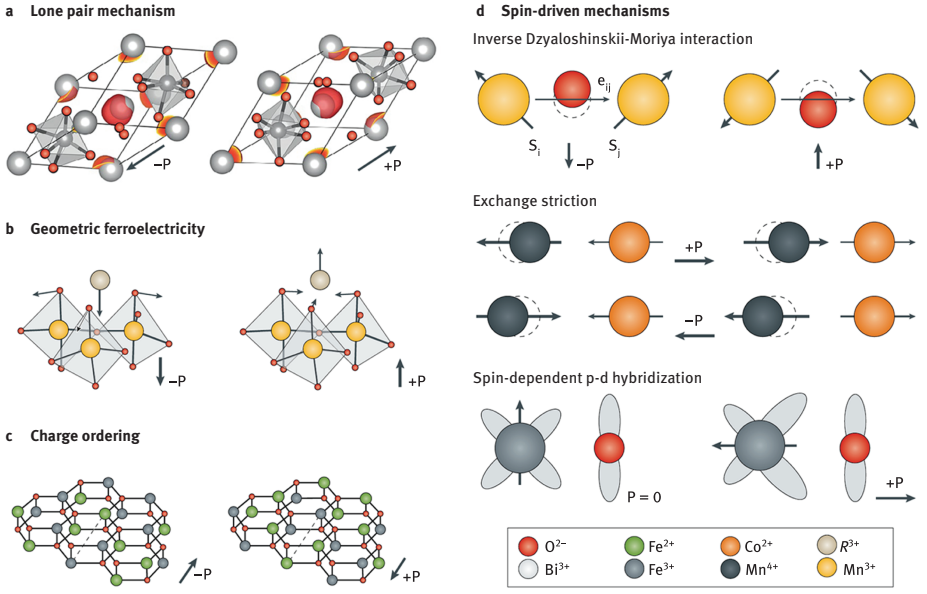

Figure 2: Classification of multiferroic materials. (a) Lone-pair mechanism: In $BiFeO_3$, two electrons shift away from the Bi^{3+} ion and towards the FeO_6 octahedra. This *lone pair* (illustrated by the red isosurface of the electron localization function) induces a spontaneous polarization, *P*, in the [111] direction. (b) Geometric ferroelectricity: Movements of the MnO_5 bipyramids in h-*R*MnO_3 lead to a displacement of the *R*-ions (indicated by black arrows), which leads to a ferroelectric polarization along the [001] axis [41]. (c) Ferroelectricity due to charge ordering: Alternating layers with Fe^{2+}/Fe^{3+} ratios of 2:1 and 1:2 were proposed to give rise to a spontaneous electric polarization in $LuFe_2O_3$ [42]. (d) Magnetically induced ferroelectricity: The inverse Dzyaloshinskii–Moriya interaction can lead to a canting of neighbouring magnetic spins, S_i and S_j, and thereby drive a polar displacement [43] as illustrated at the top (example: orthorhombic $TbMnO_3$ [33]). Alternatively, ferroelectricity can arise due to symmetric spin exchange as in Ca_3CoMnO_6 (middle) [44] or spin-driven modulations in chemical bonding (bottom) like in $CuFeO_2$ [45]. The Figure is reprinted with permission from Springer Nature, taken from [12]. Copyright 2016 by Springer Nature.

valence electrons do not participate in chemical sp-hybridized states and create a local dipole, leading to a macroscopic spontaneous electric polarization in the order of 100 μC/cm^2 [47] . The polarization is the primary symmetry breaking order parameter, classifying $BiFeO_3$ as a *proper* ferroelectric. Antiferromagnetic G-type order with an additional long-range modulation and a small canted moment arises below $T_N = 643$ K in $BiFeO_3$ [20]. With this, $BiFeO_3$ has been holding the record for single-phase materials for more than half a century, exhibiting a large electric polarization and robust magnetoelectric coupling at room temperature. Interestingly, $BiFeO_3$ is still the only established system of its kind and all attempts to achieve

further multiferroics of lone-pair type failed, including most promising candidates such as $BiMnO_3$ [48, 49].

Size effects and geometrical constraints can cause structural instabilities that lead to polar distortions and **geometric ferroelectricity** (Figure 2(b)). In h-$RMnO_3$, for example, a unit-cell-trimerizing lattice distortion is the driving force of the ferroelectric phase transition ($T_C \geq 1000$ K, $P \approx 6$ μC/cm^2) [41, 50–53]. As the primary order parameter is not the electric polarization, h-$RMnO_3$ are referred to as *improper* ferroelectrics. Magnetic ordering emerges independently and only at much lower temperatures ($T_N \approx 100$ K) [54]. Very similar behaviour is observed in the hexagonal ferrites, $RFeO_3$, with the additional advantage of a larger spin moment and room-temperature magnetism [55, 56]. The emergence of room-temperature multiferroicity in h-$RFeO_3$ is appealing, but strong magnetoelectric couplings at technologically relevant length scales, i.e. at the level of domains, are yet to be demonstrated. Another interesting material with geometric ferroelectricity is $BaNiF_4$, where an asymmetry of Ba^{2+} and F^- sites induces ferroelectricity [57, 58]. Although the geometric ferroelectricity in $BaNiF_4$ is too small to be of use for device applications (≈ 0.01 μC/cm^2), it is of profound interest as it involves weak magnetic order that can be reversed by switching the electric polarization.

Charge carriers can localize and form a non-centrosymmetric superlattice, leading to **ferroelectricity due to charge ordering** (Figure 2(c)). Long-range magnetic order and, hence, multiferroicity may arise at a separate phase transition [59]. $LuFe_2O_4$ is considered the role model for charge-order driven multiferroicity, but even after one decade of research the emergence of ferroelectricity is called into question and continues to stimulate controversial debates [42, 60]. Mixed manganites, such as $Pr_{1-x}Ca_xMnO_3$, $Y_{1-x}Ca_xMnO_3$, and $Pr(Sr_{0.1}Ca_{0.9})_2Mn_2O_7$ were discussed as well, but did not attract broader attention [59]. By all indications, charge-order driven multiferroicity is an elegant concept of strong academic interest but will not help us to design competitive functional materials.

Another way to induce acentricity in otherwise centrosymmetric structures is magnetism, which can lead to a spontaneous electric polarization and hence multiferroicity. By definition, **magnetically induced ferroelectricity** is *improper* (or *pseudoproper*) and, in many materials, originates from magnetic frustration. Non-centrosymmetric spin textures due to competing magnetic interactions evolve, for example, in Cr_2BeO_4, $TbMnO_3$, $MnWO_4$, $Ni_3V_2O_8$, $CoCr_2O_4$, and CuO [see, e.g. [9] for a review]. The non-centrosymmetric magnetic order gives rise to the so-called inverse Dzyaloshinskii-Moryia (DM) interaction [43, 61]. Enabled by relativistic spin-orbit coupling, the low magnetic symmetry is projected onto the crystal lattice and induces a small polar displacement. The orientation of the displacement is determined by the chirality of the spin system ($S_i \times S_j \neq 0$), which yields a unique one-to-one correlation between the (antiferro-)magnetic order and the electric polarization [61, 62]. Successful ongoing attempts to achieve larger polarization (> 0.1 μC/cm^2 [63]), higher ordering temperature [64–66], and viable thin film architectures [67] reflect a

substantial potential for further development and correlation phenomena that are yet to be harnessed. The inverse DM interaction is the most intensively studied microscopic mechanism that leads to magnetically driven ferroelectricity but it is certainly not the only one. In the delafossites $CuFe_{1-x}Rh_xO_2$ ($0 \le x \le 0.15$) a spontaneous polarization of about 0.2 μC/cm^2 is induced by a screw-like spin structure ($S_i \times S_j = 0$), being driven by a complex combination of spin-orbit interaction and spin helicity [45]. Inherently larger polarization values arise in collinear magnets with non-relativistic Heisenberg-like exchange striction ($\propto S_i \cdot S_j$), such as YMn_2O_5 [68, 69], orthorhombic $HoMnO_3$ [70], and the spinel CdV_2O_4 [71]. Up to now, however, ferroelectricity due to collinear magnetism has only been observed at low temperature so that technological applications remain elusive.

In summary, comparing multiferroics with ferroelectricity driven by different mechanisms, $BiFeO_3$ and its lone-pair mechanism (Figure 2(a)) is still most promising when it comes to device applications. However, the pool of multiferroics with ferroelectricity due to lone-pairs has never widened since the discovery of $BiFeO_3$ in the 1960s. In contrast, the number of spin-driven multiferroics recently exploded and robust room-temperature systems with significantly improved electric and magnetic properties appear to be within reach. Thus, given the current development, it is reasonable to say that spin-driven multiferroicity may play an equally important role and possibly even dethrone the lone-pair mechanism in the future.

3 What's next?

The revival of multiferroics [12, 72, 73] during the second era led to a comprehensive understanding of the mechanisms that facilitate coexisting electric and magnetic order (Figure 2), as well as conceptually new design strategies for device architectures [67, 74, 75]. Thus, this era brought us an important step closer to multiferroic-based technology. Although the research field has truly matured over the last two decades, the race for *ideal* multiferroics is still on and scientists keep searching for the perfect material that enables low-energy electric field control of magnetism at room-temperature. In addition, research efforts that were used to focus on multiferroics are now expanding into other fields, ranging from basic cosmology-related questions [76] to novel concepts that may revolutionize information and communication technologies [77].

It is thus a perfect time to take a step back and recap what we already know about the basics of multiferroicity, available model materials, as well as opportunities for next-generation technology. For this purpose, key aspects related to the fundamentals and applications of multiferroics are reviewed in a comprehensive series of topical articles. Here, recent developments in different multiferroics are discussed, covering materials where electric and magnetic order emerge independently (type I) in DOI:10.1515/PSR.2019.0014 and DOI:10.1515/PSR.2019.0070, or

jointly (type II) in DOI:10.1515/PSR.2019.0016 and DOI:10.1515/PSR.2019.0071. Other articles from the series review the characterization of multiferroics at macro- and nanoscopic length scales (DOI:10.1515/PSR.2019.0015, DOI:10.1515/PSR.2019.0068), novel materials (DOI:10.1515/PSR.2019.0069) and excitations (DOI:10.1515/PSR.2019.0055, DOI:10.1515/PSR.2019.0017), as well as domain and domain wall related phenomena (DOI:10.1515/PSR.2019.0067) and recent progress in thin films for device applications (DOI:10.1515/PSR.2019.0072).

On the one hand, the series of topical reviews is of interest for specialists to keep an overview of key discoveries within the field, despite the exploding number of publications on multiferroics. On the other hand, the comprehensive collection of articles can serve as a solid foundation for students and newcomers who are just entering the field. Because one thing is clear: the exciting journey that once started with ferroelectromagnets is by far not over yet. In fact, the third era – which will take us the beyond the classical multiferroics research as we know it from the past – is just beginning. First intriguing precursors associated with this third era of multiferroics are, for example, non-trivial topological textures such as magnetoelectric skyrmions [78, 79] and hybrid domain walls [80, 81], higher-order correlation phenomena at the level of domains [82] and emergent chemical phases at the nanoscale [83].

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