

A Brief Review on Magnetoelectric Multiferroic Oxides

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(Received April 5, 2021; Revised April 7, 2021; Accepted April 7, 2021)

Abstract: Magnetoelectric multiferroics, where a ferromagnetic and a ferroelectric order coexist and are coupled in a single phase, have been a hot topic in condensed matter physics for a long time owing to their ability to facilitate next-generation applications. In this review, we briefly introduce basic concept of the magnetoelectric multiferroic oxides as well as their history, physical origins, and significant achievements. The key moments contributing to the progress of magnetoelectric multiferroics are snapshotted chronologically, and then a discussion on the major magnetic exchange interactions and the ferroelectric origins are presented along with their coupling behavior. Furthermore, we argue a need for modifying the present classification of magnetoelectric multiferroics before presenting the evolution of multiferroics using representative examples with their properties such as magnetic/ferroelectric transition temperature, magnetization/electric polarization, and magnetoelectric coefficient. We hope that this brief review will provide the community researchers with insights into magnetoelectric multiferroic oxides.

Keywords: Multiferroics, Magnetoelectric coupling, Ferromagnetism, Ferroelectricity

1. INTRODUCTION

Ferroc properties, *i.e.*, ferromagnetism, ferroelectricity, and ferroelasticity, are some of the oldest known physical phenomena and have attracted interest in both fundamental physics and practical applications [1,2]. Among the diverse array of ferroic research, their coexistence and coupling have generated a considerable interest for decades. Multiferroicity was initially defined as the coexistence of more than two ferroic properties in a single phase, although the definition has been extended to include anti-ferroic properties such as antiferromagnetism; this conceptual stretching is due to the conflicting origins of ferromagnetism and ferroelectricity.

The coupling between ferroic properties is a rather different concept from their coexistence in that an order parameter is controlled by the other, which makes this field more intriguing than before. For example, much interest in multiferroics manifesting ferroelectricity and ferroelasticity in a single phase stems not from their coexistence but from their coupling behavior, *i.e.*, electric-field-induced deformation and mechanical-strain-induced polarization [3-6].

In this study, we focused on magnetoelectrically active multiferroicity in a single phase owing to their fascinating and novel behaviors. Magnetoelectric (ME) coupling, the so-called ME effect or response, is a phenomenon that indicates that spontaneous electric polarization can be switched by an applied magnetic field (direct ME coupling) and magnetic spins can be aligned by an applied electric field (converse ME coupling). In this sense, an ME coupling could be induced in ferromagnetic/piezoelectric composites, and even in (anti)ferromagnetic oxides possessing an unconventional

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ferroelectric origin owing to spin-driven ferroelectricity; nevertheless, research into this topic is still limited.

Since the coexistence of ferroelectricity and antiferromagnetism along with magnetic-field-induced ME coupling has been demonstrated in epitaxial BiFeO₃ thin films [7] and TbMnO₃ single crystals [8], ME multiferroic oxides have attracted much attention, leading to extensive studies. Unfortunately, it is generally accepted that the magnetic spins of antiferromagnetic oxides are more difficult to manipulate than those of ferromagnetic oxides in terms of general uses and the generation of a satisfactory ME coefficient at room temperature, preventing their use in many potential applications, *e.g.*, ME RAM [9-11], logic devices [12], photovoltaics [13-15], cell detectors [16-18], and drug delivery systems [19,20]. Thus, much research in recent years has focused on developing appropriate single-phase multiferroic materials exhibiting the coexistence and the coupling of soft ferromagnetism and displacive ferroelectricity at ambient temperatures through the discovery of unusual mechanisms such as d^0 magnetism [21] or non- d^0 ferroelectricity [22].

In this review, we present a brief overview of ME multiferroic oxides from the perspective of historical progress, physical origins, and representative examples. Furthermore, we explore the classification of ME multiferroics by emphasizing their coupling phenomena.

2. HISTORY OF MAGNETOELECTRIC COUPLING AND MULTIFERROICITY

The first discussion of the correlation between magnetic and electric properties was in 1888 by Röntgen, who found that a dielectric material tends to be magnetized while being passed under an electric field [23]; an intrinsic correlation was then considered in 1894 by Curie [24]. The term “magnetolectric” was coined in 1926 by Debye [25], which was 68 years earlier than the first use of the term “multiferroic” by Schmid in 1994 [26]. In 1960, there were three significant achievements in the field of ME. First, Landau introduced a mathematical formulation of the ME effect [27], which will be discussed in section 3. Second, Dzyaloshinskii theoretically predicted that a linear relationship between magnetic and electric behaviors (so-called linear ME coupling) could

occur in Cr₂O₃ [28]. Finally, this relationship was experimentally demonstrated by Astrov and Folen in Cr₂O₃ single crystals, where antiferromagnetic behavior and ME coupling were manifested at 307 K [29,30]. Nevertheless, these results could not bring about a turning point for ME research due to weak coupling behavior ($\alpha_{ME} \sim 3.5$ ps/m at 250 K). To enhance the ME coefficient for use in practical applications, Van Suchtelen (1972) suggested the use of a composite structure consisting of magnetostrictive and piezoelectric phases, *i.e.*, mechanical strain-mediated ME coupling [31]. Although strain-mediated ME coupling generates a sufficient ME coefficient, its architecture restricts the range of its uses for controlling magnetic spins with an electric field or implementing into small-scale applications. This warrants the needs for developing ME multiferroics on single phase materials.

In 2000, Spaldin debated the scarcity of magnetoelectrically coupled multiferroics in her highly cited review paper entitled “Why are there few magnetic ferroelectrics?” [32]. She found the answer from several fundamental reasons. Firstly, in the view of the crystal symmetry groups, there are only 13 point-groups which could exhibit both magnetization and spontaneous electric polarization. She suggested that the number of considered point groups is small enough to significantly narrow down the candidates for multiferroic properties in a single phase. Secondly, the electric behavior of these properties is completely different; it is generally accepted that ferroelectricity is a property of insulating materials, whereas magnetic materials generally exhibit inherent conductivity. Thus, it is difficult to find materials with the moderate electrical conductivity required to exhibit magnetism and ferroelectricity at the same time. Finally, the lack of multiferroics can be explained by their incompatible d -orbital occupancy. It is noted that magnetic behavior, for example, ferromagnetism and antiferromagnetism, originates from the arrangement of localized magnetic spins possessing a net moment that comes from unpaired electrons sitting at the d and the f orbitals. In contrast, the d^0 orbital plays an important role in the conventional ferroelectricity of perovskite oxides, as it forms a covalent bond with the p orbital of oxygen ion, which causes cations to be off-centered, resulting in a spontaneous electric polarization. Her argument was so pertinent that the retarded progress on the desired goal of

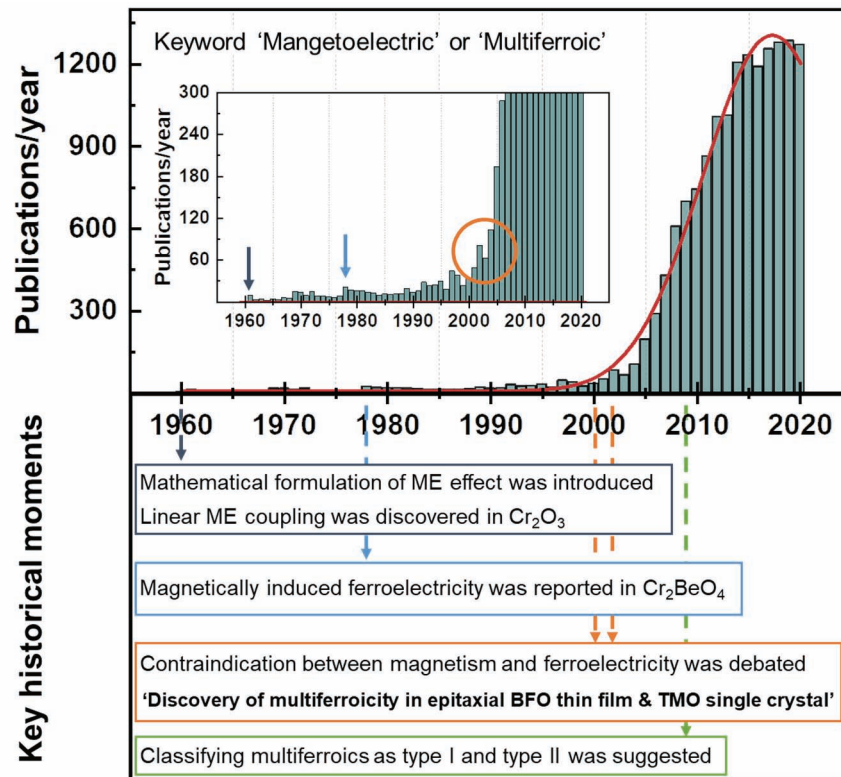


Fig. 1. Number of publications per year with 'magnetoelectric' or 'multiferroic' as keywords according to Web of Science™ (<https://apps.webofknowledge.com>).

developing room-temperature ME coupled multiferroics between a ferromagnetism and a ferroelectricity was considered unavoidable. Reversely, however, we may say that this seemingly implausible fundamental situation allows us to use her analyses as a guideline for developing single-phase multiferroics in that once the restrictions forced by her analyses were overcome, ultimately desired room-temperature single-phase ME coupled multiferroics could be realized.

In fact, historic experimental results were presented by Wang et al. and Kimura et al. in 2003, resulting in a sharp increase in the number of publications on multiferroics, as shown in Fig. 1. Wang et al. demonstrated the coexistence of displacive ferroelectric and antiferromagnetic properties at room temperature in an epitaxially grown BiFeO_3 (BFO) multiferroic thin film [7], while Kimura et al. reported that ferroelectric polarization can be controlled by magnetic field on single-crystalline TbMnO_3 (TMO) [8]. In addition to these discoveries, there are many notable publications that demonstrate ME multiferroicity in other materials, as will be

discussed in section 4, such as double perovskites [33,34], orthorhombic/hexagonal manganese perovskites [35-38], and Ruddlesden-Popper compounds [39] as well as Y/Z type hexaferrites [40,41], and spinel ferrites [42-44]. Currently, various methods for developing ME multiferroics have been proposed for non-oxide materials such as 2D materials [45,46], bromides [47], and fluorides [48], indicating that much research still focuses on the discovery of new room-temperature single-phase multiferroics with a substantial coupling between soft-ferromagnetism and displacive-ferroelectricity.

It should be noted that in 2009, Khomskii categorized multiferroics as type I and type II based on the origin of their ferroelectricity [49]. The proposed scheme is most commonly used in this field to categorize the findings because it can simply classify materials just in terms of 'multiferroics' depending on the absence or the presence of spin-induced ferroelectricity. However, there remains some confusion in terms of 'ME coupling', which is a more fascinating and key

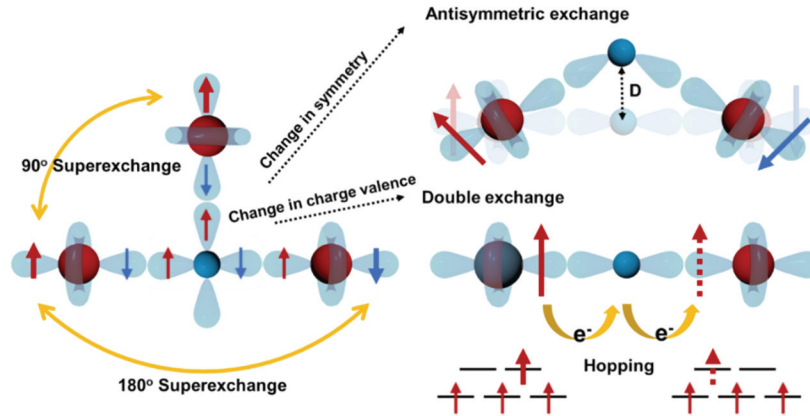


Fig. 2. Schematic illustration of magnetic exchange interactions occurring in oxides.

phenomenon than their coexistence, implying that the classification needs to be improved by reflecting the state of multiferroics research.

3. PHYSICAL ORIGINS

Generally, multiferroicity involves breaking time reversal and spatial inversion symmetries, which causes ferromagnetism and ferroelectricity, respectively [50]. Although these origins were noticed a long time ago, research based on these facts has indicated that it is difficult to combine two ferroic properties for several reasons. In this regard, understanding their complex and subtle intricacies should precede the development of ME multiferroics. Hereinafter, we will briefly introduce the physical origins of each property — exchange interactions for magnetism, ways to break centrosymmetry for ferroelectricity, and ME coupling — which are useful in understanding the nature and the classification of ME multiferroics.

3.1 Magnetism and spin exchange interactions

It is well known that magnetism is classified as ferro-, ferri-, antiferro-, para-, or diamagnetism based on the existence and the arrangement of spins, which are determined by exchange interactions between localized spins originating from unpaired electrons sitting at *d* and *f* orbitals. This means that manipulating the exchange interaction plays a key role in the

development of ferromagnetic behavior accompanying ME coupling. Therefore, we introduce basic theories on the magnetic spin exchange interactions which are frequently mentioned in multiferroic oxide studies.

The exchange interaction is based on the Heisenberg exchange Hamiltonian equation as follows:

$$\hat{H}_{ex} = -\sum_i \sum_{j \neq i} J_{ij} \vec{S}_i \cdot \vec{S}_j \quad (1)$$

where J_{ij} is the exchange integral, which is a sensitive term for the orbital states, and $\vec{S}_{i,j}$ is related to the spin vector operator [51]. Spin exchange interactions in magnetic oxides can be sorted into three main classes depending on the inter-spin distance [52-54]: intra-atomic exchange, which occurs between electrons in the same orbital (Hund's first rule); direct exchange, which is defined as an interaction between the nearest neighboring atoms; and superexchange, which indicates the interplay of two transition metals (TM) via an intermediary anion. Among them, the superexchange interaction, the so-called symmetric exchange, is the dominant mechanism in magnetic oxides because the existing O ion acts as an intermediary between TMs. It is noted that the superexchange interaction is affected by magnetic spin moments and their interaction angle, as explained by the well-established Goodenough-Kanamori-Anderson (GKA) rules [55-57]. From the GKA rules, the superexchange interaction with a 180° TM-O-TM angle creates an antiferromagnetic spin arrangement, whereas a 90° angle results in ferromagnetic behavior. For example, BiFeO₃ is constrained to an antiferromagnetic spin arrangement because of its atomic configu-

ration; all TMs are located at the B site and aligned in a straight line, forcing a 180° superexchange between the Fe ions via O ions (Fe-O-Fe symmetric exchange interaction). In this way, the 180° superexchange interaction prevents many multiferroic oxides from possessing ferromagnetic properties that allow easier manipulation of magnetic spin arrangements and higher saturation magnetization values than antiferromagnetism.

We introduce several spin exchanges derived from interactions, such as superexchange, which are useful for understanding ME multiferroicity in oxide materials. First, *antisymmetric exchange* [Dzyaloshinskii–Moriya (DM) interaction] was first discussed by Dzyaloshinskii to resolve doubts about the weak ferromagnetism of α -Fe₂O₃ [58,59]. He argued that a net magnetic moment could be induced in a direction perpendicular to the trigonal axis in-between canted spins, that is, antisymmetric spin configuration contrary to superexchange (symmetric exchange), using the following equation:

$$\hat{H}_{DM} = D_{ij} \cdot (S_i \times S_j) \quad (2)$$

where D is a constant vector. Thus, spin canting generates a net magnetic moment even in α -Fe₂O₃ according to the DM interaction. It is noted that the inverse DM interaction is the most common origin of type II multiferroics, resulting in spin-orbit coupling that breaks the centrosymmetric configuration. The second spin exchange interaction is known as *double exchange*, which has a symmetric spin configuration similar to that of superexchange [60]. A distinct feature of this exchange interaction is the existence of TMs with unequal charge valence, which results in delocalized electron hopping between interactive TMs via O, as shown below in an equation created by Zener [61].

$$\hat{H}_{DE} = \frac{2t_{TM,O}^2}{U} (S_i \cdot S_j) \quad (3)$$

where t is the hopping energy between the TM and O, and U is the Hubbard energy. He suggested that these hopping electrons reduce the exchange energy state, allowing spin alignment in the same direction, that is, ferromagnetic arrangement. This suggestion was supported by the correlation between electric conductivity and ferromagnetism, as presented by Jonker and Van Santen [62]. This interaction is generally

explained by referring to the case of manganese oxides possessing an itinerant electron in the Mn³⁺-O²⁻-Mn⁴⁺ exchange interaction, which could be the origin of spin-charge coupling and will be discussed in the next section. Finally, *exchange striction* is not an exchange interaction, but a phenomenon caused by direct exchange between d orbitals, or kinetic and potential exchange interactions via both $2p$ and $2s$ orbitals, as observed in magnetic oxides such as NiO and MnO [63-67]. The exchange magnetoelastic energy is expressed by adding a second term to the direct exchange interaction equation to include exchange-induced deformations of the lattice constant and inter-spin distance.

$$\hat{H}_{ES} = j(S_i \cdot S_j) - j(S_i \cdot S_j)^2 \quad (4)$$

In the case of the kinetic exchange accompanying the potential exchange, the equation is expressed as below:

$$J_k = -\frac{2b^2}{U} \quad (5)$$

where b is the transfer integral term, which is dependent on the angle and inter-distance between spins, and U is the energy required for an electron to move between cations. This phenomenon can be easily understood by thinking of inherent magnetic spin, which aligns along a magnetic field direction; attraction forces occur between spins in the same direction, while repulsion between spins in the opposite direction. The inter-spin forces of attraction and repulsion resulting from these exchange interactions could be the origin of spin-lattice coupling by inducing lattice deformations.

3.2 Proper and improper ferroelectricity

Ferroelectricity is specific to dielectrics, exhibiting spontaneous electric polarization that can be switched by an external electric field; both piezoelectric and pyroelectric behavior are involved. After the first example of ferroelectricity was observed in Rochelle salt in 1921 by Valasek, the theories of conventional ferroelectricity [68], the so-called displacive or proper ferroelectrics originating from the lone pair electrons in Pb²⁺ or Bi³⁺ ion or empty d^0 orbital, are well established [69]. *Lone-pair ferroelectricity* is generally observed in Bi- or Pb-based perovskite oxides, where existing electrons in the $2s$ orbital along with the $2p$ orbital in O re-

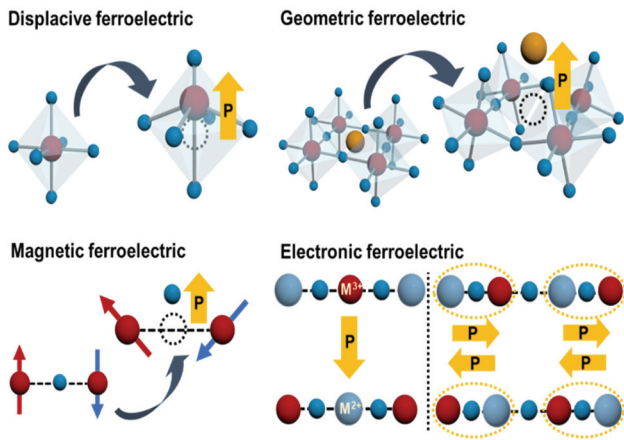


Fig. 3. Schematic illustration of the mechanisms promoting ferroelectric behavior.

sult in particularly oriented electric dipoles through an *sp*-hybridization. For example, BiFeO₃ is considered the most attractive multiferroic material, exhibiting a high ferroelectric Curie temperature ($T_{C,FE}$, 1,103 K) and a large spontaneous polarization ($>100 \mu\text{C}/\text{m}^2$) [7,70]. The prominent ferroelectric nature of BiFeO₃ originates from the off-center displacement of Bi³⁺ in the cuboctahedral oxygen cage; in other words, the centrosymmetric configuration is broken through orbital hybridization between the $6s^2$ orbital in Bi ion and the $2p$ orbital in O. Similarly, *d⁰-ness ferroelectricity* also results from atomic displacement, but through covalent bonding between the d^0 orbital of the TM located at the B site and the p orbital in O in the ABO₃ perovskite structure. BaTiO₃ is a representative *d⁰-ness* ferroelectric oxide with a notable dielectric constant along with a high $T_{C,FE}$ (403 K), and considerable spontaneous polarization ($\sim 25 \mu\text{C}/\text{m}^2$) [71]. Density functional theory (DFT) calculations have demonstrated the role of covalent bonding between d^0 and p orbitals through double-well potential energy, which determines the position of the TM sitting at the B site surrounded by the octahedral O cage [72,73].

In recent years, however, anomalous phenomena that cannot be explained by the existing theories have been reported; thus, the following new mechanisms have been proposed the so-called improper ferroelectrics [74]. First, a *geometric ferroelectricity* arises from a structural instability, which breaks the centrosymmetric configuration [75]. For example, rotational distortion of O cages generates a driving force that

results in the movement of atoms located between polyhedra. This situation can be observed in hexagonal perovskites such as YMnO₃, where the Y ion could be displaced through the driving force (long-range dipole–dipole interactions, MnO₆ polyhedra buckling, and a small amount of rehybridization phenomenon) capacitating the structural transformation between the ferroelectric and paraelectric phases depending on the electric field [38,76]. Therefore, in this atomic configuration, electric polarization is generated with a specific orientation along a certain axis, which is the same direction as the Y ion off-centering. Despite the high $T_{C,FE}$ ($\sim 1,200$ K), YMnO₃ has a smaller spontaneous polarization ($\sim 5 \mu\text{C}/\text{m}^2$) than that of proper ferroelectrics owing to its weak driving force [36,77,78]. Secondly, an *electronic ferroelectricity* occurs by bond- and site-centered charge ordering, which leads to a localized electric polarization along a certain orientation [79–82]. In the case of bond-centered charge ordering, the electric polarization is induced through atomic dimerization originating from the difference in bonding strength between atoms having the same charge number. In contrast, in the case of site-centered charge ordering, an electric polarization originates from a heterogeneous charge configuration, where atoms are aligned at the same intervals but have different charge numbers. Both charge orderings were exemplarily demonstrated in Pr_{1-x}Ca_xMnO₃ (bond- and site-centered charge ordering at $x = 0.4$ and 0.5 , respectively) [83,84]. Finally, a *magnetic ferroelectricity* has been widely recognized as a universal mechanism for developing spin-driven type II multiferroics because an electrically polarized state can be manipulated by magnetic spin exchange interaction (*i.e.*, DM interaction), leading to the breaking of the centrosymmetric configuration [85–87]. Owing to the prevalence of the DM interaction, many magnetic ferroelectrics have been discovered (*e.g.*, Cr₂O₃, orthorhombic perovskite, and spinel ferrite); however, there remains a limitation on their ferroelectric properties owing to the weak driving force for the symmetry breaking interaction. This mechanism will be discussed in further detail with reference to ME coupling and the status of magnetoelectrical research.

3.3 Magnetoelectric coupling

As outlined above, the ME effect describes the coupling between spontaneous polarization (P) and magnetic field (H),

as well as between magnetization (M) and electric field (E), as expressed by the following free energy, F:

$$F(\vec{E}, \vec{H}) = F_0 - P_i^s E_i - M_i^s H_i - \frac{1}{2} \epsilon_0 \chi_{ij}^e E_i E_j - \frac{1}{2} \mu_0 \chi_{ij}^m H_i H_j - \alpha_{i,j} E_i H_j - \frac{1}{2} \beta_{ijk} E_i H_j H_k - \frac{1}{2} \gamma_{ijk} H_i E_j E_k - \dots \quad (6)$$

where ϵ_0 and μ_0 are the (electric and magnetic, respectively) permittivity of the free space, $\chi^{e,m}$ is the (electric and magnetic, respectively) susceptibility, α is the linear ME coefficient term, and β and γ are non-linear (quadratic) ME coefficient factors. In this equation, each polarization and magnetization can be derived through differentiation.

$$P_i(\vec{E}, \vec{H}) = P_i^s + \epsilon_0 \chi_{ij}^e E_j + \alpha_{i,j} H_j + \frac{1}{2} \beta_{ijk} H_j H_k + \gamma_{ijk} H_i E_j - \dots \quad (7)$$

$$H_i(\vec{E}, \vec{H}) = M_i^s + \mu_0 \chi_{ij}^m H_j + \alpha_{i,j} E_i + \beta_{ijk} E_i H_j + \frac{1}{2} \gamma_{ijk} E_j E_k - \dots \quad (8)$$

Finally, the linear ME coefficient, α_{ME} , which is the most frequently mentioned in magnetoelectric research field, can be obtained from the following equations:

$$\alpha_{ME}^H = \left(\frac{\partial P}{\partial H} \right) \quad (9)$$

$$\alpha_{ME}^E = \left(\frac{\partial M}{\partial E} \right) \quad (10)$$

([s/m] in SI units)

In addition to the above equations, the ME voltage coefficient ($\alpha_{ME,V}$) should also be considered because it is a useful

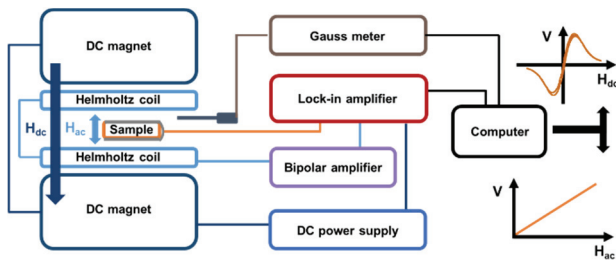


Fig. 4. Schematic diagram presenting the measurement system for magnetoelectric coupling.

parameter in the evaluation of compatibility for potential applications (the measurement system is shown in Fig. 4).

$$\alpha_{ME,V}^H = \left(\frac{\partial E}{\partial H} \right) = \frac{1}{t} \left(\frac{\partial V}{\partial H} \right) \quad (11)$$

where V is the voltage and t is the thickness of the sample. Given that $P = \epsilon_0 \chi E = \epsilon_0 (\epsilon_r - 1) E \cong \epsilon_0 \epsilon_r E$, where ϵ_r is the relative permittivity ($\gg 1$), we can derive the relation between the ME coefficient and ME voltage coefficient as follows:

$$\alpha_{ME}^H = \left(\frac{\partial P}{\partial H} \right) = \epsilon_0 \epsilon_r \left(\frac{\partial E}{\partial H} \right) = \frac{\epsilon_0 \epsilon_r}{t} \left(\frac{\partial V}{\partial H} \right) = \epsilon_0 \epsilon_r \alpha_{ME,V}^H \quad (12)$$

([V/A] in SI units and [V/cm·Oe] in CGS units)

We now introduce three mechanisms of ME coupling in a single phase, skipping a detailed explanation of the measurement techniques thanks to many previous studies [88-90]. *Spin-charge coupling* is expected to play a major role in developing a strong spin-driven ME coupling by considering their origins, where both magnetization and polarization in this case depend on the electronic carrier density, that is, the activity of itinerant electrons. For example, LuFe2O4 is a representative frustrated charge ordering system, where the average valence state is 2.5, because of the randomly distributed Fe ions in its double-layer structure [91,92]. This indicates that extra electrons travel freely between the Fe ions in this

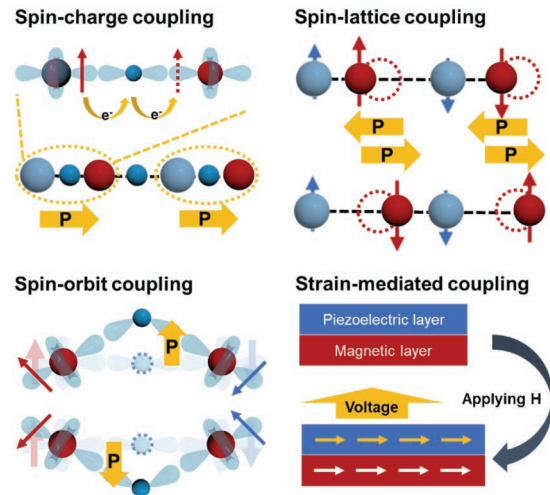


Fig. 5. Schematic illustration accounting for magnetoelectric coupling for each coupling case.

composition. This material has drawn attention in the development of room-temperature multiferroics owing to its prominent ferroelectric properties ($T_c=330$ K, $\sim 27 \mu\text{C}/\text{m}^2$) compared to other improper ferroelectrics, although its low Néel temperature ($T_N=120$ K) remains to be improved. Secondly, *spin-lattice coupling* typically originates from attraction and repulsion between magnetic spins. This is largely due to the exchange striction, which is explained by the direct exchange interaction combined with the magnetic dipole-dipole interaction which is related to the spin direction and inter-distance between two magnetic dipoles [93]. The electric polarization originating from spin-lattice coupling is expressed as follows:

$$P \sim -\frac{\chi_l}{2V} \sum_{i,j} J'_{i,j} (S_i \cdot S_j) \quad (13)$$

where χ_l is the dielectric susceptibility related to the polar lattice mode and V is the system volume. We provide an example of this coupling by presenting TbMnO_3 , which has a cycloidal spiral spin configuration below 27 K under atmospheric pressure. When a pressure of 4~5 GPa is applied to the sample, the spin arrangement can be converted into a collinear up-up-down-down spin configuration, known as an E-type antiferromagnetic structure. In this situation, the forces of attraction and repulsion are intensified through the interplay of each up-up and up-down spin arrangement owing to the direct exchange interaction, which is linked to the spin direction and interatomic displacement. As a result, an electric polarization ($1 \mu\text{C}/\text{cm}^2$) larger than that of pristine TbMnO_3 ($0.1 \mu\text{C}/\text{cm}^2$) is generated, which originates from the inverse DM interaction [94]. Finally, *spin-orbit coupling* is the most familiar mechanism, known as the inverse DM interaction (precisely, they are not the same) and involving many representative multiferroics, such as Cr_2O_3 , BiFeO_3 , and TbMnO_3 . It is suggested that spin canting in the inverse DM interaction causes the off-center displacement of O ions originally located at the center between TMs in the symmetric exchange. Thus, spin canting in magnetic oxides could lead to electric polarization by breaking the symmetric configuration of the TM-O-TM bond, as explained by the spin current model [the so-called Katsura-Nagaosa-Balatsky (KNB) model] [95-97].

$$P \sim e_{i,j} \times (S_i \times S_j) \quad (14)$$

where P is the electric polarization, and $e_{i,j}$ is the unit vector relating the two spins. Given that the electric polarization arising from the inverse DM interaction is sensitive to the magnetic field due to its origin, spin-orbit coupling has generated significant interest despite its weak ferroelectric properties.

Although the focus of this review is single-phase ME multiferroics, we also discuss composite ME coupling due to its significance and for a comparison purpose. As previously mentioned, *magnetostrictive-piezoelectric strain-mediated coupling* can be revealed in a composite consisting of magnetostrictive and piezoelectric materials [98]; thus, understanding the nature of magnetostrictive and piezoelectric materials should precede the discussion of strain-mediated ME composites. Magnetostrictive materials exhibit magneto-elastic coupling, where the volume changes depending on the magnetic field due to the arrangement of magnetic domains. Similarly, piezoelectric materials manifest electro-elastic coupling that an electric voltage is generated through the volume deformation. The sequence of strain-mediated ME coupling is as follows: the volume of a magnetostrictive material is manipulated depending on the magnetic domain, which is aligned along a particular direction by an applied magnetic field, and immediately the volume of piezoelectric materials deforms following that of the magnetostrictive material. Finally, ME voltage is generated in the piezoelectric material owing to its inherent properties. Thus, the connectivity and interfacial bonding between distinct materials play an important role in the enhancement of the ME voltage coefficient. The configuration of ME composites was initially limited to layered discs or cantilevers; nowadays, various structures, such as core-shell structures and multilayered thin films, are used [90,99,100]. Although the ME composite generates a much larger ME voltage than the single phase, it is restricted to be used in applications which require a small scale and direct coupling with a high response speed.

4. CLASSIFICATION OF MAGNETOELECTRIC MULTIFERROICS

As discussed previously, discovering new materials and novel mechanisms for ME multiferroicity remains a current topic. Before we summarize the current state of research, the

classification of multiferroics, type I and type II, as described by Khomskii in 2009 [49] should be rediscussed. The following is direct quotes from Khomskii, so as to convey his intent as it is. He said, “*The first group, which can be called type-I multiferroics, contains those materials in which ferroelectricity and magnetism have different sources and appear largely independently of one another, though there is some coupling between them.*”, and next, “*The second group, which we can call type-II multiferroics, is the relatively recently discovered materials, in which magnetism causes ferroelectricity, implying a strong coupling between the two.*”. Therefore, it is generally accepted that single-phase multiferroics exhibiting completely different origins of magnetism and ferroelectricity are categorized as type I, while those manifesting (anti)ferromagnetism and magnetic ferroelectricity are classified as type II. This categorization provided a clear criterion for classifying single-phase multiferroic materials at the time. It should be noted that classifying ME multiferroics as type I or II is not an absolute criterion. When the origins of ME coupling and recently discovered multiferroics were considered, questions arose around this classification. For example, BiFeO₃ (BFO) has been widely recognized as a type I multiferroic material owing to its differing ferroic origins. However, its ME coupling solely originates from antisymmetric spin exchange, indicating that embedded magnetic ferroelectricity exists and BFO can be classified as a type II multiferroic. We infer that the reason for adopting the previous classification—where ME multiferroics are

grouped by considering the absence or the presence of an independent ferroelectric origin—is the scarcity of materials exhibiting the coexistence of ferromagnetism and ferroelectricity, contrary to other multiferroics manifesting the coexistence of ferroelectricity and ferroelasticity. Further, the need for an additional type or a new classification system is increasing as more and more unusual single-phase ME multiferroics are discovered (see section 4.3). Hence, it is reasonable that the previous classification should be reconsidered to meet more important criteria and reflect this progress. Given that coupling is a more attractive phenomenon than coexistence, as mentioned in the introduction, it makes sense to classify ME multiferroics based on their coupling origin such as spin-charge (SCC), spin-lattice (SLC), and spin-orbital (SOC) coupling types. Nevertheless, this would need a consensus with further discovery of ME multiferroic collections; thus, we, for the moment, briefly introduce representative ME multiferroic oxides based on the conventional classification owing to its universality.

4.1 Type I multiferroics

BiFeO₃ based perovskite structure: BFO is the most famous type I multiferroic owing to its high ferroelectric Curie (1,103 K) and Néel (643 K) temperatures. It was predicted even before 2003 that BFO would exhibit prominent ferroelectric properties and weak ferromagnetic behavior originating from a lone pair of Bi ions and an antisymmetric exchange between Fe ions (G-type magnetic structure), respectively. Nevertheless, BFO did not receive attention because of the non-negligible leakage current and the difficulty in fabrication avoiding secondary phases until Wang et al. produced a well-made epitaxial BFO thin film [7]. They reported a clear ferroelectric hysteresis loop ($P_s \sim 60 \mu\text{C}/\text{cm}^2$) without leakage current contribution along with a saturated magnetic hysteresis loop ($M_s \sim 150 \text{ emu}/\text{cm}^3$) in a BFO thin film constructed as a monoclinic phase different from the BFO bulk, which has a rhombohedral structure. Since then, many BFO-based studies have been reported such as rare-earth substitution [101-108], the formation of a morphotropic phase boundary through other perovskite oxide substitutions or the mechanically strained [109-111], investigating the domain wall motion [112,113], and theoretical explanations [114-116].

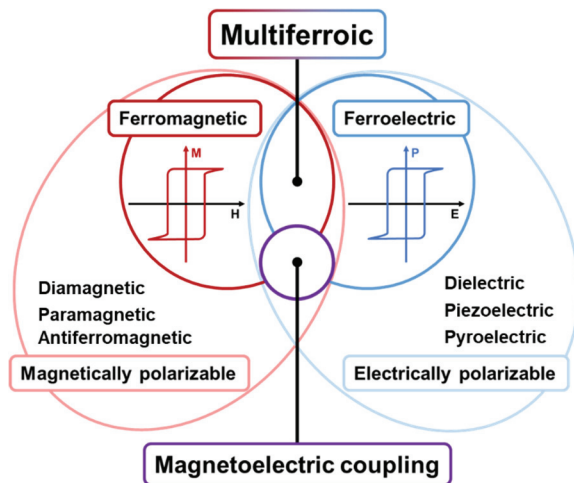


Fig. 6. Venn diagram for defining magnetoelectric multiferroics.

Lead-iron double perovskite structure, Pb_2FeMO_6 : This group includes $Pb(Fe_{1/2}Nb_{1/2})O_3$ (PFN), $Pb(Fe_{1/2}Ta_{1/2})O_3$ (PFT), and $Pb(Fe_{2/3}W_{1/3})O_3$ (PFW) [117,118], and their multiferroic properties stem from the same ferroelectric and magnetic mechanisms as BFO, that is, lone pair ferroelectricity and antisymmetric exchange along with some contribution from double exchange. However, their ferroelectric and magnetic properties are unsatisfactory ($T_{C,FE} = 380$ K and $T_N = 150$ K for PFN and $T_{C,FE} = 180$ K and $T_N = 380$ K for PFW) [33,118-120]. This multiferroic group was intensively studied by the San Juan–Cambridge–Belfast collaboration, involved by the late Scott, demonstrating a considerable ME multiferroicity through intentionally modulated structural softening. They are also called relaxor-type multiferroics and exhibit at least one relaxor ferroic characteristic [121,122]; this is evidenced by two equations: the Vogel-Fulcher equation, which was adopted for relaxors as dipolar glass, and a semi-empirical expression for the maximum dielectric constant. Although the mechanism of relaxor ferroic oxides is not yet fully understood, their inherent properties, e.g., weak ferromagnetic properties above T_N and diffuse phase transformation confirmed by the temperature-dependent dielectric permittivity, could be explained by several models such as polar nanoregions (ferroelectric relaxor) and spin glass (magnetic relaxor).

Aurivillius structure, $(Bi_2O_2)(A_{n-1}B_nO_{3n+1})$, where n is the number of octahedral layers: The Aurivillius phase is a type of perovskite structure including bismuthate layers, first referred to as Aurivillius in 1949 [123]. $Bi_{3.25}La_{0.75}Ti_3O_{12}$ (BLT) is a conventional ferroelectric Aurivillius compound, where geometric ferroelectrics originate from the distorted octahedra accompanied by an off-center displacement of the B cations within the ab-plane along a certain direction. BLT is considered a promising candidate for ferroelectric memory even as its pristine form due to its considerable spontaneous polarization ($P_s \sim 25 \mu C/m^2$) along with the high $T_{C,FE}$ (~ 950 K) [124,125]. BLT is also a noticeable material in the field of multiferroics, when TMs are introduced [126,127]. For example, $(Fe_{0.5}Co_{0.5})_xNb_x$ substituted BLT, i.e., $Bi_{3.25}La_{0.75}Ti_{3-2x}(Fe_{0.5}Co_{0.5})_xNb_xO_{12}$ ($x = 0.05, 0.25, \text{ and } 0.35$), was shown to possess a weak ferromagnetism (0.5 emu/g at 300 K) with the ME coefficient of $\sim 0.6 \text{ mV/cm}\cdot\text{Oe}$ at 100 K, when textured. Their ME multiferroic properties are driven by a 180° superexchange interaction (Fe-O-Co) involving antisymmet-

ric exchange depending on the magnetic field, which results in a spin-orbital coupling, that is, the inverse DM interaction.

Hexagonal rare-earth ferrite and manganite, $h\text{-RMO}_3$ ($R = \text{rare earth and } M = Mn, Fe$): $h\text{-RMO}_3$ exhibits type I multiferroicity through the coexistence of geometric ferroelectricity and antiferromagnetism; it should be noted that hexagonal RMO_3 is different from orthorhombic RMO_3 , which is classified into a type II multiferroic despite the identical chemical composition. Generally, these structures can be modulated to transform into each other depending on the stability of the crystal structure, which is affected by various conditions, such as the atomic size difference between R and M, the type of substrate in the thin film, and the degree of pressure. $h\text{-YMnO}_3$, which is already referred to as a geometric ferroelectric, is a representative $h\text{-RMO}_3$ multiferroic, and its antiferromagnetic properties originate from 120° triangular Mn-O-Mn bonding below $T_N \sim 70$ K [38,128]. Analogously, $h\text{-Lu}_{0.5}\text{Sc}_{0.5}\text{FeO}_3$ and $h\text{-LuFeO}_3$ are type I multiferroics having the same mechanism as $h\text{-YMnO}_3$ and exhibiting higher antiferromagnetic order; $h\text{-Lu}_{0.5}\text{Sc}_{0.5}\text{FeO}_3$ presents the $T_{C,FE}$ of $1,050$ K and the T_N of 440 K [129,130]. Given that the driving force of geometric ferroelectrics is well linked to the inverse DM interaction, which depends on the change in the bond length and the angle of exchange interaction, a strong coupling coefficient is expected in this group. The ME coefficient is not yet clearly understood in terms of magnetic-field-dependent spin behavior but has a considerable value, e.g., $\sim 2 \text{ mV/cm}\cdot\text{Oe}$ in $h\text{-YMnO}_3$, and $0.5 \text{ mV/cm}\cdot\text{Oe}$ in $h\text{-Lu}_{0.5}\text{In}_{0.5}\text{FeO}_3$ [130,131].

Other ferroelectric perovskite oxides: Since the discovery of epitaxial BFO thin films, many attempts have been made to convert conventional ferroelectrics into ME multiferroics by introducing TMs or rare earth metals. Some examples of these materials include Fe-doped $Ba(Ti,Zr)O_3$ [132], $(Ba_{1-x}Sm_x)(Ti_{1-x}Fe_x)O_3$ [133], $BaTi_{1-x}Ni_xO_3$ [134], $Na_{0.42}Bi_{0.52}Ti_{1.005}O_3$ [135], Mn-doped $Bi_{0.5}Na_{0.5}TiO_3$ [136], $(Bi_{0.5-y/2}Na_{0.5-y/2})(Ti_{1-y}Fe_y)O_3$ [137], and $K_{0.5}Na_{0.5}(Nb_{1-x}Fe_{x/2}Co_{x/2})O_3$ [138]. In addition, theoretical predictions and explanations for ME multiferroicity in perovskite oxides have been extensively studied. As such, many studies have been published which suggest that type I multiferroicity arises from compositional substitution in ferroelectric perovskite oxides; however, there are many unqualified results in the demonstration of magnetic and ferroelectric hysteresis loops.

4.2 Type II multiferroics

Orthogonal rare-earth ferrite and manganite, o-RMO₃ (R = rare earth and M = Mn, Fe): TbMnO₃ (TMO) is the representative example of type II multiferroics [8]. The multiferroic properties of o-TMO depend entirely on spin configurations in response to temperature and magnetic field at atmospheric pressure, where magnetic spins can be randomly oriented (paramagnetic), longitudinally arranged below 41 K (sinusoidal state, antiferromagnetic), and transversely modulated below 28 K (cycloidal state, antiferromagnetic) [139,140]. This is evidenced by the fact that the transition temperature of the ferroelectricity ($P_s \sim 0.04 \mu\text{C}/\text{cm}^2$ at 10 K with a magnetic field strength of 9 T) is consistent with that of the antisymmetric spin exchange, indicating that $T_{\text{C,FE}}$ and T_{N} are the same. 12 years after the demonstration of magnetic-field-induced ME coupling (direct ME coupling) by Kimura et al., electric-field-induced ME coupling (converse ME coupling) was also confirmed by Matsubara et al. by imaging multiferroic domain wall motion [141].

Hexaferrite (Y-type and Z-type): Hexaferrites are one of the best-known ferromagnetic materials with sufficient $T_{\text{C,FM}}$. It should be noted that various arrangements of TMs within different types of hexaferrites result in various spiral magnetic structures such as cycloidal, longitudinal conical, proper screw, and transverse conical structures, all of which exhibit type II multiferroicity. We introduce Y- and Z-types as type II multiferroics; among six hexaferrite types, the origin of multiferroicity is unclear in M-types (as will be discussed), and multiferroicity is not well established in the other types. Since Kimura et al. discovered the magnetic-field-induced electric polarization in Y-type hexaferrite (Ba_{0.5}Sr_{1.5}Zn₂Fe₁₂O₂₂), it has been extensively studied because of its considerable ME coefficient at a low magnetic field. It should be noted that a large ME coefficient is observed in Ba_{0.4}Sr_{1.6}Mg₂Fe₁₂O₂₂ single crystal with a value of 33,000 ps/m at 10 K [142]. Given that a pristine BaMg₂Fe₁₂O₂₂ undergoes a magnetic phase transition step by step, that is, two-fold, four-fold, and incommensurate spin arrangements depend on an applied magnetic field. The key point of the large ME coefficient in this system is the one-step sharp transition from a stabilized two-fold transverse cone by Sr substitution. In other words, a dramatic change in spin canting leads to massive electric polarization. In the case of Z-type hexaferrite,

Kitagawa presented the low-field ME effect in Sr₃Co₂Fe₂₄O₄₁ polycrystalline ceramics sintered in oxygen atmosphere, where the electric polarization was $P_s \sim 1 \times 10^{-3} \mu\text{C}/\text{cm}^2$ at 0.25 T [41]. Multiferroic hexaferrites are still attracting much attention due to their diverse constituents having a potential to manifest an excellent ME multiferroicity.

Spinel ferrite, AB₂O₄: Spinel structures consisting of tetrahedral (T_d) and octahedral (O_h) sites are also well-known magnetic oxides with ferromagnetic or antiferromagnetic behavior depending on the kind and the spin configuration of the TM introduced (*i.e.*, inverse ($[\text{B}]_{\text{tet}}[\text{A},\text{B}]_{\text{oct}}\text{O}_3$) and normal ($[\text{A}]_{\text{tet}}[\text{B},\text{B}]_{\text{oct}}\text{O}_3$) spinel structures). Unlike the case of hexaferrites, spin-driven ferroelectricity in spinel ferrites is attributed to various origins (such as inverse DM interaction, exchange striction, and *p-d* hybridization) depending on their composition. For example, the origin of the electric polarization in CoCr₂O₄ is in line with hexaferrite, that is, the inverse DM interaction combined with the spin current model, as evidenced by many previous studies [43]. It is well known that normal spinel CoCr₂O₄, where $T_{\text{C,FE}}$ is 93 K, exhibits an incommensurate conical spin arrangement at temperatures below its critical point (T_s , 26 K), and produces an electric polarization of $P_s \sim 15 \times 10^{-4} \mu\text{C}/\text{cm}^2$ at a magnetic field strength of 2 T. In the case of normal spinel CdV₂O₄, a cubic-tetragonal transition that occurs at ~ 95 K forces up-up-down-down spin arrangement below T_{N} (33 K) through antisymmetric V-O-V bonding accompanied by dimerization between V ions, which plays an important role in inducing electric polarization ($P_s \sim 5 \times 10^{-4} \mu\text{C}/\text{cm}^2$ at 15 K) through exchange striction [143]. Similarly, the structural phase transition in inverse spinel NiFe₂O₄ gives rise to type II multiferroicity. The *p-d* hybridization between Fe and O ions in the tetragonal NiFe₂O₄ generates electric polarization with a significant value of $P_s \sim 0.25 \mu\text{C}/\text{cm}^2$ for a 5 kV/cm electric field (<80 K), as validated by experimental results [144-146]. However, this value is significantly lower than the theoretical value ($P_s \sim 23 \mu\text{C}/\text{cm}^2$) obtained from DFT calculations, even considering the calculation was done at 0 K.

Tenorite, CuO: Kimura et al. discovered type II multiferroicity in CuO, where geometrically frustrated spins generate a large electric polarization ($P_s \sim 15 \times 10^{-3} \mu\text{C}/\text{cm}^2$ at 220 K) with a high T_{N} of 230 K [147]. He provided a new multiferroic class, *i.e.*, binary multiferroic oxides, where an incommensurate spiral spin arrangement is constructed between

213 (T_{N1}) and 230 K (T_{N2}) and demonstrated the potential of spin-driven multiferroics.

Other type II multiferroics: In addition to the aforementioned materials, many intriguing studies have been reported on other materials such as $\text{Ba}_2\text{CoGe}_2\text{O}_7$ [148], CoAl_2O_4 [149], $\text{Co}_4\text{Nb}_2\text{O}_9$ single crystals [150], CuFeO_2 [151], $\text{Cu}_2\text{V}_2\text{O}_7$ [152], DyCrO_4 [153], $\text{Ho}_x\text{La}_{3-x}\text{Ga}_5\text{SiO}_{14}$ [154], $\text{La}_{1-x}\text{Ca}_x\text{MnO}_3$ [83,155,156], LiFe_5O_8 [157], Mn_2GeO_4 [158], RFeWO_6 [159], TbMn_2O_5 [160,161], and YBaCuFeO_5 [162,163]. Although type I materials are known to exhibit an excellent performance in terms of ferroelectric properties, type II multiferroics are more important due to their fascinating mechanisms which plays a key role in the development of ME coupling.

4.3 Other single phase magnetoelectric multiferroics

Hexaferrite (M-type): M-type hexaferrite, that is, $\text{AFe}_{12}\text{O}_{19}$ ($\text{A} = \text{Ba}, \text{Sr}, \text{and Pb}$), is a well-known hard-ferromagnetic oxide, exhibiting considerable saturation magnetization (60 emu/g) along with a high $T_{C,FM}$ (730 K). The origin of ferroelectricity in these materials is not clear but several explanations have been suggested such as the inverse DM interaction and the local electric dipoles originating from the off-center displacement of Fe^{3+} [164,165]. Moreover, incongruous electric polarization, which confuses its ferroelectric origin, was measured by Tan et al. who has been researching multiferroics since 2010 [166-168]. He suggested that the electric polarization and transition temperature from ferroelectric to antiferroelectric be estimated to be $P_s \sim 80 \mu\text{C}/\text{cm}^2$ by an applied electric field and 595 K, respectively. Since all suggestions were supported by experimental and theoretical results, it is difficult to categorize this group into a specific type, because there is not sufficient rationale to classify them as one type over the other. Nevertheless, intense research should continue because M-type hexaferrite is one of the major candidates for room-temperature multiferroics. In addition to M-type hexaferrite, there are many new discoveries whose origin of ME multiferroicity cannot be categorized clearly nor well defined by conventional theories, such as *BaMnO₃* [22], *layered perovskites* [169], and *polar magnetic oxides* (e.g., *Cation-ordered corundum*, and *Brownmillerite*) [170].

4.4 Composite magnetoelectric multiferroics

Atomically engineered (LuFeO₃)_m/(LuFe₂O₄)₁ superlattice series for 1 ≤ m ≤ 10: Mundy et al. reported atomically engineered $(\text{LuFeO}_3)_m/(\text{LuFe}_2\text{O}_4)_1$ superlattices using reactive-oxide molecular-beam epitaxy [171]. The existence of a self-doped structure, where Fe^{3+} and Fe^{2+} are arranged in bilayers with 2:1 ratio, plays a key role in the enhancement of both ferromagnetic and ferroelectric behaviors in these superlattice series ($T_{C,FM} = 281 \text{ K}$ and $T_{C,FE} = 1020 \text{ K}$ in $(\text{LuFeO}_3)_9/(\text{LuFe}_2\text{O}_4)_1$). This was evidenced by magnetic circular dichroism combined with DFT calculations. In addition, they observed ME coupling at 320 K using X-ray magnetic circular dichroic photoemission electron microscopy on the Fe L₃ edge, demonstrating that enhanced ME multiferroicity originates from a charge transfer between Fe^{2+} and Fe^{3+} [172]. Thus, the origin of the ME multiferroicity in this superlattice is completely different from the strain-mediated ME coupling in usual composites, even though it is categorized as a composite owing to its layered configuration.

Magnetostrictive/piezoelectric strain-mediated ME composites: The state-of-the-art strain-mediated ME composites should be discussed by classifying magnetostrictive materials (Fe , FeCo , $\text{Tb}_{1-x}\text{Dy}_x\text{Fe}_2$, $\text{Ni}_{1-x}\text{Zn}_x\text{FeO}_4$, etc.), piezoelectric materials ($\text{Pb}(\text{Zr,Ti})\text{O}_3$, $\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3$ - PbTiO_3 , BaTiO_3 , etc.), phase connectivity modes (2-2, 0-3, etc.), and interfacial types (core-shell, nanowires, etc.) [98,173,174]. Given that there are several pieces of good review papers on the topic [90,175,176] and the topic itself is beyond the scope of this brief review, we do not discuss this in detail here.

5. CONCLUSIONS

In this short review, we provide a brief overview of the progress in the development of single-phase ME multiferroics from various points of view. ME multiferroics are still attracting considerable interest owing to their fascinating nature from the perspective of their physical properties and potential applications. Unfortunately, the progress to date still seems far from the goal specifically in terms of realizing their wide range of applications, based on their reported physical properties, for example, impractically low magnetic and ferroelectric transition temperatures, the absence of

strong coupling between displacive ferroelectricity and soft ferromagnetism, impractical fabrication methods for industry use. Although there may be many other minor hindrances as well as already-known paradoxes, we supposed that the main reason for the stagnation in the development of room-temperature single-phase ME multiferroic oxides is the limitation of manipulating the magnetic exchange interaction in displacive ferroelectric perovskite oxides. It is generally accepted that a displacive ferroelectric, manifesting a larger electric polarization than an improper ferroelectric, arises in perovskite oxides (ABO_3), where TMs are located at the B site imposing 180° superexchange interaction via O ions. This means that they are inherently confined to exhibit less useful antiferromagnetic properties, which makes it difficult to induce a considerable ME coupling at room temperature. In this regard, manipulating the magnetic exchange path in ferroelectric perovskite oxides might be a major breakthrough in achieving this goal; however, this method is known to be restricted by the Goldschmidt tolerance factor. Interestingly, in contrast to prior understanding, the design of 90° superexchange interaction within a double perovskite structure has been successfully demonstrated in recent years. The A-site-engineered magnetoelectrically active perovskite reveals not only the coexistence of soft-ferromagnetism and displacive ferroelectricity at room temperature but also direct coupling between them [177]. In addition, many interesting publications have recently been updated to demonstrate ME multiferroics based on a new mechanism breaking conventional concepts such as magnetism in the d^0 orbital and ferroelectricity in the non- d^0 orbital. Given that the scarcity of multiferroic materials has been resolved to some extent owing to recent achievements, intense research should continue by focusing on the direct coupling phenomenon between ferroelectric and ferromagnetic materials at ambient temperatures. An immediate application of such material would be for voltage-driven magnetoelectric random access memories and magnetic-field-controlled cell detectors.

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ACKNOWLEDGEMENTS

This research was supported by the Leading Foreign Research Institute Recruitment Program (No.2017K1A4A3015437) through the National Research Foundation of Korea (NRF) funded by Ministry of Science and ICT and the 2021 Research Fund (1.210035.01) of UNIST (Ulsan National Institute of Science and Technology).

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