



Fig. 1. Relationship between multiferroic and magnetoelectric materials, illustrating the requirements to achieve both in a material (adapted from Ref. [14]).

that form the underpinnings for both advanced technologies (such as ferroelectric nonvolatile memories, SONAR, transformers, etc.) and a wealth of basic science (for example in the colossal magnetoresistant (CMR) manganites). Such a broad range of responses can be enabled within a framework of the oxygen coordination octahedron, by simply changing the cationic occupations of the A- and B-sites. The interplay between the electronic and ionic structure of the cations at the A- and B-sites as well as their ionic sizes, leads to the rich diversity of structural derivatives of the basic simple cubic structure, manifesting in the many types of physical responses. Over the past several years, the exploration of these individual functional responses has evolved into the exploration of coupled order, namely the existence of multiple order parameters, as exemplified by multiferroics. From the investigation of bulk single crystals to novel characterization techniques that probe order parameters, coupling, and spin dynamics this is truly a diverse field, rich with experimental and theoretical complexity. By definition, a single phase multiferroic [12] is a material that simultaneously possesses two or more of the so-called “ferro” order parameters – such as ferroelectricity, ferromagnetism, and ferroelasticity. Magnetoelectric coupling typically refers to the linear magnetoelectric effect manifested as an induction of magnetization by an electric field or polarization by a magnetic field [13]. The overlap required of ferroic materials to be classified as multiferroic is shown schematically in Fig. 1 [14]. Only a small subgroup of all magnetically and electrically polarizable

materials are either ferromagnetic or ferroelectric and fewer still simultaneously exhibit both order parameters. The ultimate goal for device functionality would be a single phase multiferroic with strong coupling between ferroelectric and ferromagnetic order parameters, enabling simple control over the magnetic nature of the material with an applied electric field at room temperature. Some possible pathways to multiferroic behavior are presented in Table 1.

### 3.1. The model multiferroic, $\text{BiFeO}_3$

There are several pathways available to create coupled order parameters; these are summarized in recent reviews [15,16]. In this review, we will focus specifically on the  $\text{BiFeO}_3$  system, since this is essentially the only single-phase multiferroic that simultaneously possesses both magnetic and ferroelectric order at and above room temperature – prompting unprecedented research and study by the multiferroics community. The perovskite  $\text{BiFeO}_3$  was first produced in the late 1950s [17] and many of the early studies were focused on the same concepts important today – the potential for magnetoelectric coupling [18]. Throughout the 1960s and 1970s much controversy surrounded the true physical and structural properties of  $\text{BiFeO}_3$ , but as early as the 1960s it was suspected to be an antiferromagnetic, ferroelectric multiferroic [19,20]. The true ferroelectric nature of  $\text{BiFeO}_3$ , however, remained somewhat in question until ferroelectric measurements made at 77 K in 1970 [20] revealed a spontaneous polarization of  $\sim 6.1 \mu\text{C cm}^{-2}$  along the 111-direction, consistent with the rhombohedral polar space group  $R3c$  determined from single crystal X-ray diffraction [21] and neutron diffraction studies [22]. These findings were confirmed by detailed structural characterization of ferroelectric/ferroelastic monodomain single crystal samples [18]. The structure of  $\text{BiFeO}_3$  can be characterized by two distorted perovskite blocks connected along their body diagonal or the pseudocubic  $\langle 111 \rangle$ , to build a rhombohedral unit cell (Fig. 2a) [23]. In this structure the two oxygen octahedra of the cells connected along the  $\langle 111 \rangle$  are rotated clockwise and counterclockwise around the  $\langle 111 \rangle$  by  $\pm 13.8(3)^\circ$  and the Fe ion is shifted by 0.135 Å along the same axis away from the oxygen octahedron center position. Such large spontaneous distortions should normally be accompanied

Table 1

Summary of pathways to multiferroic order in materials including various Types I and II routes and prototypical materials.

	Pathway to	Mechanism for multiferroism	Examples
Type I	A-site driven	Stereochemical activity of A-site lone pair gives rise to ferroelectricity and magnetism arises from B-site cation	$\text{BiFeO}_3$ , $\text{BiMnO}_3$
	Geometrically driven	Long-range dipole–dipole interactions and oxygen rotations drive the system towards a stable ferroelectric state	$\text{YMnO}_3$ , $\text{BaNiF}_4$
	Charge ordering	Non-centrosymmetric charge ordering arrangements result in ferroelectricity in magnetic materials	$\text{LuFe}_2\text{O}_4$
Type II	Magnetic ordering	Ferroelectricity is induced by the formation of a symmetry-lowering magnetic ground state that lacks inversion symmetry	$\text{TbMnO}_3$ , $\text{DyMnO}_3$ , $\text{TbMn}_2\text{O}_4$