# New routes to multiferroics

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DOI: 10.1039/b709126e

Multiferroic materials are those which possess both ferroelectric and ferromagnetic properties. Clearly, there is a contradiction here since ferromagnetism requires d-electrons while ferroelectricity generally occurs only in the absence of d-electrons. Several multiferroics demonstrating magnetoelectric coupling effects have, however, been discovered in the past few years, but they generally make use of alternative mechanisms in attaining these properties. Several new ideas and concepts have emerged in the past two years, typical of them being magnetic ferroelectricity induced by frustrated magnetism, lone pair effect, charge-ordering and local non-centrosymmetry. Charge-order driven magnetic ferroelectricity is interesting in that it would be expected to occur in a large number of rare earth manganites, $Ln_{1-x}A_xMnO_3$ (A = alkaline earth), well known for colossal magnetoresistance, electronic phase separation and other properties. In this article, we discuss novel routes to multiferroics, giving specific examples of materials along with their characteristics.

## Introduction

Materials which exhibit both magnetic and electrical ordering have attracted great interest in the past few years, partly because of their technological potential. Besides a range of possible device applications, the science of these materials is truly fascinating.[1–6] In the most general terms, multiferroics are materials in which ferromagnetism, ferroelectricity and ferroelasticity occur in the same phase. This implies that they possess spontaneous magnetization which can be reoriented by an applied magnetic field, spontaneous polarization which can be reoriented by an applied electric field and spontaneous deformation which can be reoriented by an applied stress. It is, however, customary to exclude ferroelasticity and only consider magnetic and ferroelectric characteristics. Multiferroics possess neither spatial inversion symmetry nor time-reversal symmetry.

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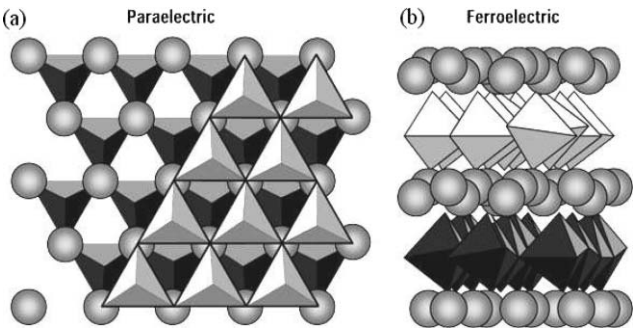


**Fig. 1** Crystal structure of $YMnO_3$ in (a) the paraelectric and (b) the ferroelectric phases.

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It is generally difficult to find materials that are magnetic as well as ferroelectric, since ferroelectricity occurs when the metal ions have empty d-orbitals. Magnetism, on the other hand, occurs in materials containing cations with partially filled d-orbitals. Magnetoelectrics are simultaneously ferromagnetic and ferroelectric in the same phase, with coupling between the two orders. Magnetoelectric coupling describes the influence of a magnetic (electric) field on the polarization (magnetization) of a material and vice versa. Magnetoelectric coupling can exist independent of the nature of the magnetic and electrical order parameters. It is an independent phenomenon which may not necessarily arise in materials that are both magnetically and electrically polarizable. Since the coexistence of magnetism and ferroelectric ordering is not favoured, materials with such properties arising from alternative mechanisms have been sought in recent years.

Many years ago, some mixed perovskites were shown to be weakly ferromagnetic and ferroelectric by Smolensky *et al.*,[7] a typical example being $(1 - x)Pb(Fe_{2/3}W_{1/3})O_3 - xPb(Mg_{1/2}W_{1/2})O_3$. Magnetoelectric switching has been known to occur in boracite, $Ni_3B_7O_{13}I$.[8] The ferromagnetic spinel $CdCr_2S_4$ exhibits relaxor ferroelectricity below 135 K.[9] $YMnO_3$ is antiferromagnetic below the Néel temperature ($T_N$) 80 K and ferroelectric below the Curie temperature ($T_{CE}$) 914 K.[10] In this material, ferroelectricity is associated with the tilting of the $MnO_5$ trigonal bypyramids. Another oxide with similar properties is $BiFeO_3$ ($T_N$ = 670 K, $T_{CE}$ = 1110 K),[11] where ferroelectricity arises from the stereochemical activity of the Bi lone pair.[12] $BiMnO_3$ is one of the few materials recently shown to be simultaneously ferromagnetic and ferroelectric ($T_C$ = 450 K, $T_{CE}$ = 105 K).[13] While $BiFeO_3$ and $BiMnO_3$ are proper ferroelectrics, $TbMnO_3$, which is an improper ferroelectric, shows interesting features wherein spiral magnetic ordering is the source of the ferroelectricity.[14] One of the new ideas is that charge-ordered and orbital ordered perovskites could exhibit ferroelectric magnetism due to coupling between magnetic and charge-ordering.[15] Beside single phase oxide materials, several two-phase systems

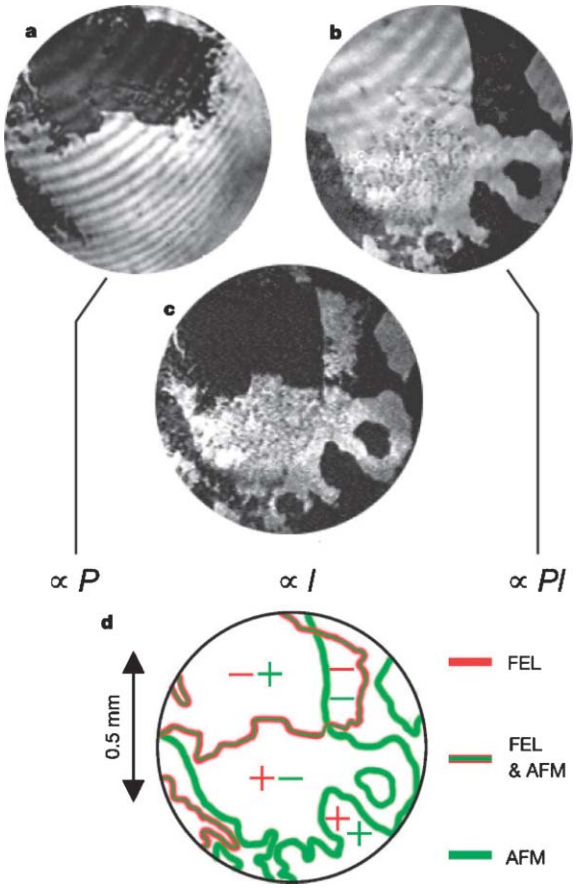


**Fig. 2** Coexistance of electric and magnetic domains in a $YMnO_3$ sample at 6 K. (a) Exposed with second harmonic light from $\chi(P)$, where $\chi$ is the nonlinear optical susceptibility and $P$ is the ferroelectric order parameter. Dark and bright areas correspond to opposite ferroelectric (FEL) domains. (b) Exposed with ferroelectromagentic (FEM) second harmonic light from $\chi(Pl)$ where $l$ is the antiferromagnetic (AFM) order parameter. Bright and dark regions are distinguished by an opposite sign of the product $Pl$. (c) Dark and bright areas correspond to opposite AFM domains. (d) Topology of FEL (red) walls and AFM (green) walls in the sample with $\pm$ signs of the corresponding colour indicating the orientation of the FEL and AFM order parameters in selected domains (from ref. 10).

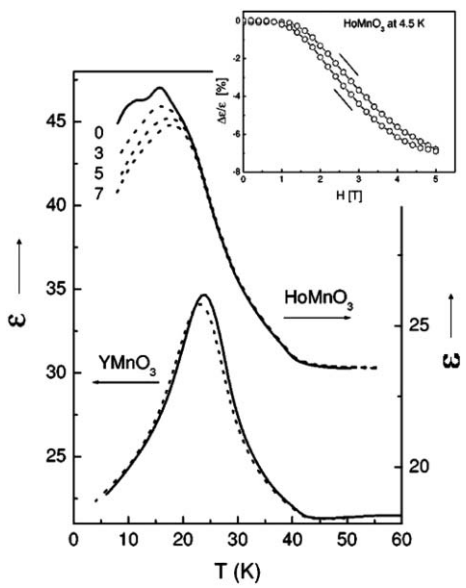


**Fig. 3** Magnetodielectric effect in $YMnO_3$ (left scale, full line: $H$ = 0; dotted line: $H$ = 7 T) and in $HoMnO_3$ (right scale, full line: $H$ = 0; dotted lines: $H$ = 3,5,7 T from top to bottom). Inset: relative change of the dielectric constant as a function of the magnetic field for $HoMnO_3$ at 4.5 K (from ref. 22).

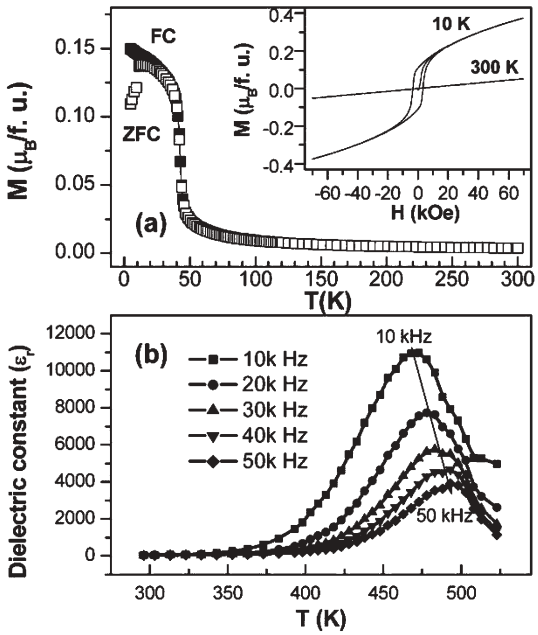


**Fig. 4** (a) Temperature variation of magnetization of $InMnO_3$ at 100 Oe. Inset shows the magnetic hysteresis loops at 10 and 300 K. (b) Temperature variation of the dielectric constant for different frequencies (from ref. 24).

have been shown to exhibit magnetoelectric coupling,[4] typical examples being $BaTiO_3$–$CoFe_2O_4$, $Tb_xDy_{1-x}Fe_2$–$Pb(Zr,Ti)O_3$ (PZT) and $La_{0.7}Sr_{0.3}MnO_3$–PZT. In this article, we restrict our discussion to the multiferroic properties of different classes of single phase materials with special attention to their special features and newer concepts.

## Rare earth manganites, $LnMnO_3$ (Ln = rare earth): polyhedral tilting and spiral magnetic ordering

Hexagonal $YMnO_3$ (space group $P6_3cm$) is a proper ferroelectric and an A-type antiferromagnet with non-collinear Mn spins oriented in a triangular arrangement. Ferroelectricity in $YMnO_3$ is driven by electrostatic and size effects unlike in other perovskite oxides, where the transition is associated with changes in the chemical bonds. Off-centring of the Mn ions is energetically unfavourable in $YMnO_3$ and ferroelectricity arises from the buckling of the $MnO_5$ polyhedra, combined with the displacement of Y ions and the layered $MnO_5$ network.[16] In Fig. 1, we show the crystal structures of the ferroelectric and paraelectric phases of $YMnO_3$. The dielectric constant and tan$\delta$ measurements near $T_N$ (80 K) indicate coupling between the two orders and a negative magnetoresistive effect increasing with cooling reaching a value up to 15% at $\sim$230 K.[17] Coupling between electric and magnetic ordering in $YMnO_3$ is accompanied by the formation of domains and domain walls (Fig. 2). Domain wall interactions are seen in spatial maps obtained by imaging with optical second harmonic generation.[10] The antiferromagnetic domain walls interact with the lattice strain (ferroelectric walls), coupling between the two being mediated by the piezomagnetic effect.[18] This lowers the total energy of the system and leads to a piezomagnetic clamping of the electric and magnetic order parameters. Neutron diffraction experiments show that the structural parameters of $YMnO_3$

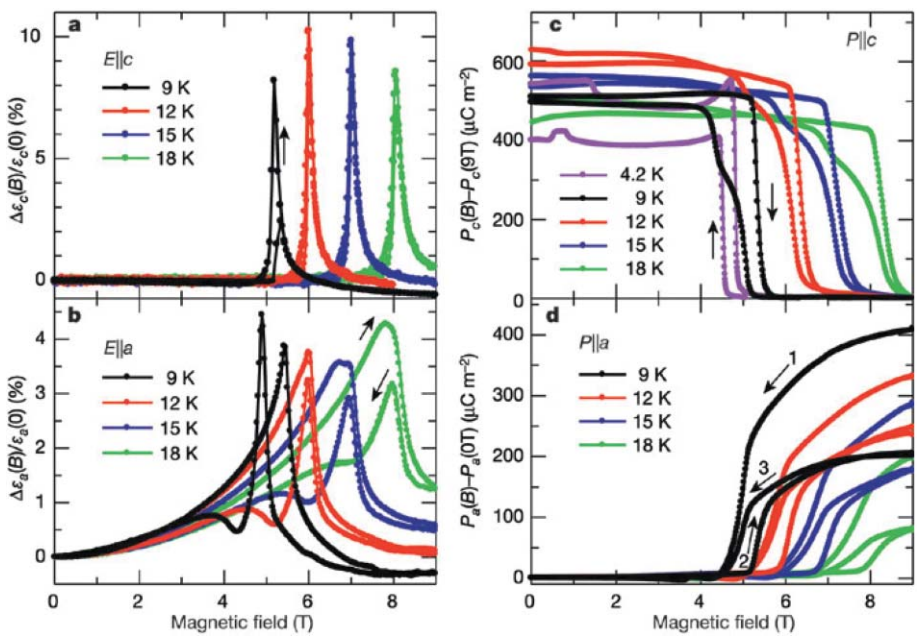


**Fig. 5** Magnetocapacitance and magnetoelectric effects in $TbMnO_3$. Magnetic field-induced change in the dielectric constant (a) and (b), electric polarization along the *c* and *a* axes, respectively (c) and (d). Magnetic fields are applied along the *b* axis. The data for (d) were collected after magnetic field cooling. The numbers in (d) denote the order of measurements at 9 K (from ref. 14).

abruptly change at $T_N$ indicating spin–lattice coupling.[19] Thermal conductivity undergoes a sudden increase upon magnetic ordering and enhances in magnitude below $T_N$.[20]

Just like $YMnO_3$, hexagonal $HoMnO_3$ also exhibits a dielectric anomaly at $T_N$ (75 K).[21] An electrically driven magnetic phase transition has also been observed in $HoMnO_3$. Orthorhombic $HoMnO_3$ and $YMnO_3$ show a large increase in the dielectric constant at $T_N$ due to strong magnetoelectric coupling (Fig. 3).[22] Hexagonal $LuMnO_3$ shows a dependence of the dielectric constant in the $T_N$ region with a weak magnetoelectric coupling. Magnetic exchange coupling in $LuMnO_3$ is mainly in the *ab* plane of the $MnO_5$ trigonal bipyramids, while the electric dipole moment of $LuO_7$ is oriented along the hexagonal *c* axis.[23] $InMnO_3$, with a hexagonal structure similar to that of $YMnO_3$, has been shown to be a canted antiferromagnet below 50 K ($T_N$) and a ferroelectric below 500 K with a small polarization (Fig. 4).[24] $InMnO_3$ is predicted to exhibit a weak piezoelectric response to uniaxial strain.

Considerable research has been carried out recently on $TbMnO_3$ and related manganites where spin frustration causes sinusoidal antiferromagnetic ordering. The collinear sinusoidal modulated magnetic structure is observed along the *b* axis accompanied by spin polarization. Large magnetocapacitance and magnetoelectric effects are observed in $TbMnO_3$ due to the switching of the electric domains by the magnetic field (Fig. 5).[14] $DyMnO_3$ shows similar properties.[25] It is interesting to compare the magnetic properties of $TbMnO_3$ and $DyMnO_3$ with those of $LaMnO_3$. In $LaMnO_3$, orbital ordering between the neighboring spins gives rise to ferromagnetic exchange in the *ab* plane and antiferromagnetic exchange along the *c* axis. Replacement of La by Tb or Dy increases the structural distortion and the next-nearest neighbor antiferromagnetic exchange frustrates the nearest neighbor ferromagnetic ordering in the *ab* plane sinusoidal collinear along the *b* axis.

## Bismuth-based compounds: lone pair effect

The properties of the bismuth compounds are largely determined by the Bi 6s lone pair.[12] $BiFeO_3$ is an incommensurate antiferromagnet and a commensurate ferroelectric at room temperature.[11,26] The spins are not collinear and take a long wavelength-spiral form and the magnetoelectric effect is, therefore, not linear and occurs in the presence of a large magnetic field[27] or by appropriate chemical substitution[28] and in epitaxial thin films.[29] $BiMnO_3$ is probably the only single phase material which is truly biferroic, but the observed polarization is small (0.12 μC $cm^{-2}$ at 87 K).[13] In Fig. 6 we show the magnetic and dielectric properties of $BiMnO_3$ along with the magnetic field-induced changes in the dielectric constant.[13,30] Ferromagnetism in $BiMnO_3$ is due to orbital ordering[31] and ferroelectric ordering is accompanied by a structural transition.[13] It has been shown recently that $BiMnO_3$ is centrosymmetric at room temperature with the centrosymmetric space group *C*2/*c*.[32] Theoretical calculations also seem to suggest a centrosymmetric structure. It is possible that this material is locally non-centrosymmetric and globally centrosymmetric. We shall

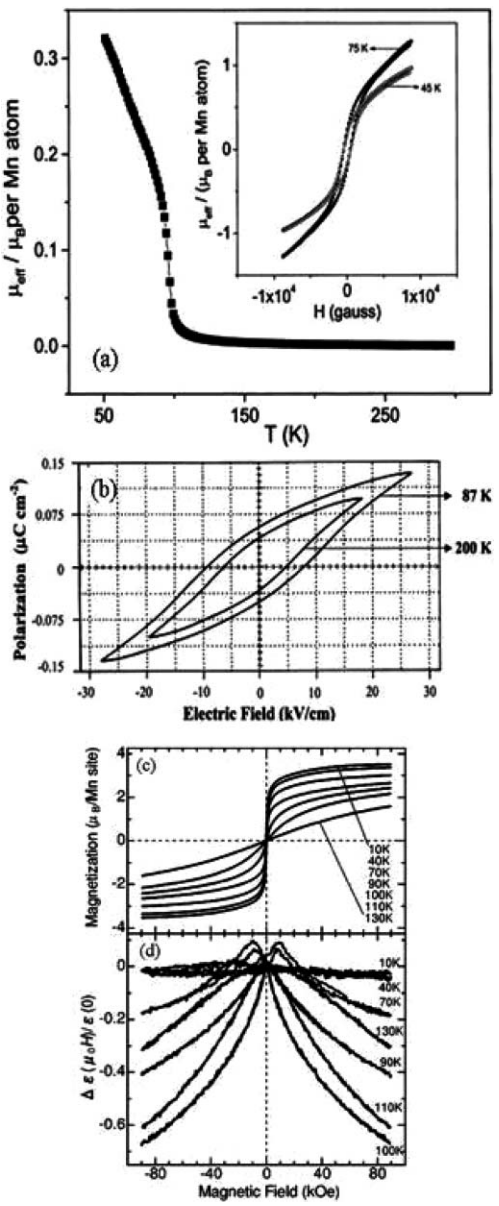


**Fig. 6** (a) Temperature variation of magnetization of $BiMnO_3$ at 500 Oe. Inset shows the hysteresis loops at 75 and 45 K, (b) *P–E* hysteresis loops of polycrystalline $BiMnO_3$ (from ref. 13). Isothermal (c) magnetization and (d) field-induced change in dielectric constant as a function of a magnetic field at different temperatures (from ref. 30).

 

discuss this aspect later when we examine rare earth chromites.

$BiCrO_3$ exhibits a ferroelectric transition at 440 K and parasitic ferromagnetism below 114 K.[33] $Bi_2Mn_{4/3}Ni_{2/3}O_6$ is a polar oxide showing a magnetic response of a concentrated spin-glass below 35 K.[34] $Bi_2MnNiO_6$ shows both the ferroelectric and ferromagnetic properties.[35] Interestingly $La_2NiMnO_6$ which is a ferromagnetic semiconductor has recently been shown to exhibit magnetocapacitance and magnetoresistance properties at temperatures upto 280 K.[36]

## $LnMn_2O_5$: frustrated magnetism

$LnMn_2O_5$ type manganites are orthorhombic solids where the $Mn^{3+}$ and $Mn^{4+}$ ions occupy different crystallographic sites, with the $Mn^{3+}$ ion at the base centre of a square pyramid and octahedrally coordinated $Mn^{4+}$ ions.[37,38] They show sequential magnetic transitions: incommensurate sinusoidal orderings of magnetic Mn spins, commensurate antiferromagnetic ordering, re-entrant transition into the incommensurate sinusoidal state and finally ordering due to rare earth spins.[39–44] These manganites exhibit electric polarization induced by collinear spin order in a frustrated magnetic system. Ferroelectricity occurs in the temperature range 25–39 K and antiferromagnetic behaviour in the range 39–45 K,[45] and the magnetic transitions are accompanied by dielectric anomalies. In a magnetic field, $DyMn_2O_5$ shows a 100% change in the dielectric constant at 3 K, and a similar behaviour is noticed in other compounds of this family as well. In $TbMn_2O_5$ the polarization is 0.04 μC $cm^{-2}$ and it is magnetically reversed.[46] The magnetic field rotates the electric polarization of $TbMn_2O_5$ by 180°. Reproducible polarization reversal in $TbMn_2O_5$ by a magnetic field is shown in Fig. 7.

## Rare earth chromites, $LnCrO_3$: role of local non-centrosymmetry

$YCrO_3$ shows canted antiferromagnetism ($T_N$ = 140 K) and a dielectric anomaly like a ferroelectric at 473 K[47] (Fig. 8). Dielectric hysteresis in $YCrO_3$ is like in leaky dielectrics with a small polarization

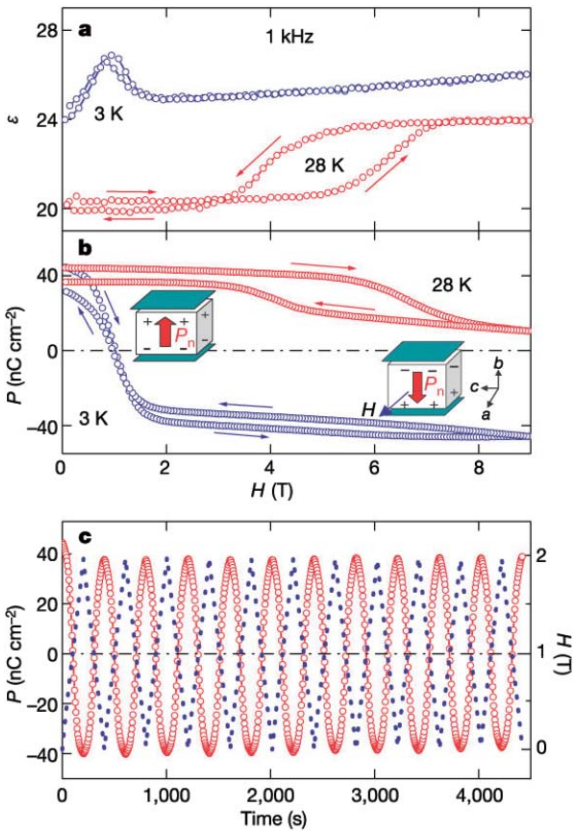


**Fig. 7** Reproducible polarization reversal in $TbMn_2O_5$ by magnetic fields. (a) Dielectric constant *versus* applied magnetic field at 3 and 28 K. (b) Change of the total electric polarization by applied magnetic fields at 3 and 28 K. (c) Polarization flipping at 3 K by linearly varying the magnetic field from 0 to 2 T. The results clearly display highly reproducible polarization switching by magnetic fields (from ref. 46).

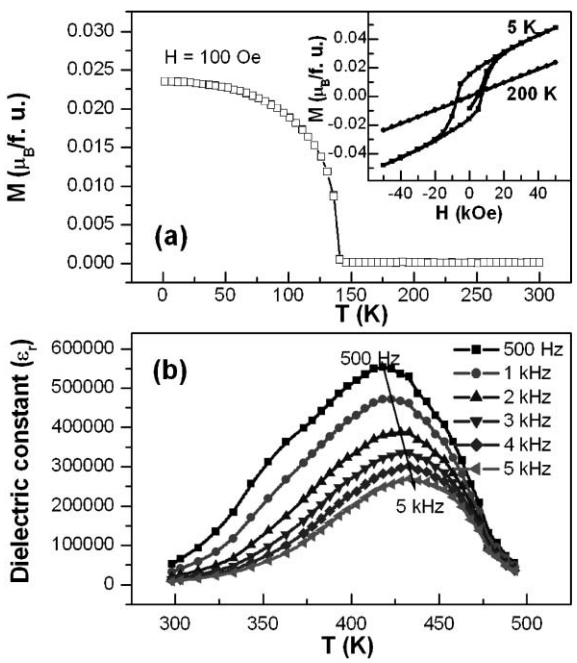


**Fig. 8** (a) Temperature variation of magnetization of $YCrO_3$ at 100 Oe. The inset shows the hysteresis loops at 5 K and 200 K. (b) Temperature variation of the dielectric constant for different frequencies (from ref. 47).

value (2 μC $cm^{-2}$). The apparent biferroic nature of $YCrO_3$ needs explanation since it is centrosymmetric with the space group *Pnma*. Local non-centrosymmetry has been proposed as the origin of ferroelectricity and interestingly careful studies of the pair distribution function (PDF) data in the 1.6–6 Å range show that the data below 473 K ($T_{CE}$) are best fitted with the non-centrosymmetric space group $P2_1$. PDF refinements over the 0–20 Å range, however, give good agreement with the centrosymmetric *Pnma* space group. The near-transition PDF data shows non-centrosymmetry below $T_{CE}$ and centrosymmetry above $T_{CE}$.[48] Typical PDF data are shown in Fig. 9. Based on these studies, it is tempting to suggest that $BiMnO_3$ could be locally non-centrosymmetric with the space group *C*2. Features of $YCrO_3$ are also shown by the heavy rare earth chromites with Ln = Ho, Er, Yb, Lu. The $T_{CE}$ increases with the decrease in the radius of the rare earth ion while the $T_N$ decreases (Fig. 10).[49]

## Magnetic ferroelectricity due to charge-ordering

Recently, Khomskii and coworkers[15] have pointed out that coupling between magnetic and charge-ordering in charge-ordered and orbital ordered perovskites can give rise to ferroelectric magnetism. Charge-ordering in the rare earth manganites, $Ln_{1-x}Ca_xMnO_3$, (Ln = rare earth) can be site-centred (SCO) or body-centred (BCO). The SCO behaviour occurs around $x = 0.5$ with a CE-type antiferromagnetic state while BCO can occur around $x = 0.4$ with a possible perpendicular spin structure. There is a report in the literature of the occurrence of a dielectric anomaly in $Pr_{0.6}Ca_{0.4}MnO_3$ around the charge-ordering transition temperature.[50] Although magnetic fields are noted to affect the dielectric properties of manganites,[51] there has been no definitive study of the effect of magnetic fields on the dielectric properties to establish whether there is coupling between the electrical and magnetic order parameters. Dielectric properties of $Pr_{0.7}Ca_{0.3}MnO_3$, $Pr_{0.6}Ca_{0.4}MnO_3$ and $Nd_{0.5}Ca_{0.5}MnO_3$ which have comparable radii of the A-site cations, and exhibit charge-ordering in the 220–240 K ($T_{CO}$) region and an antiferromagnetic transition in the 130–170 K region which have been investigated recently.[52] All these manganites exhibit dielectric constant anomalies around the charge-ordering or the magnetic transition temperatures. Magnetic fields have a marked effect on the dielectric properties, indicating the presence of coupling between the magnetic and electrical order parameters. The observation of magnetoferroelectricity in these manganites is in accord with the recent theoretical predictions of Khomskii and coworkers.[15]

It is important to note some of the important characteristics of the charge-ordered manganites in order to fully understand their ferroic properties. The most important feature is that all these manganites exhibit electronic phase separation at low temperatures ($T < T_{CO}$).[53] They exhibit a decrease in resistivity on application of large magnetic fields (>4 T).[53,54] Application of electric fields also causes a significant decrease in the resistivity of the manganites.[54,55] On the application of electric fields, the manganites show a magnetic response.[56] Such electric field-induced magnetization may also be taken as evidence for coupling between the electric and magnetic order parameters in the

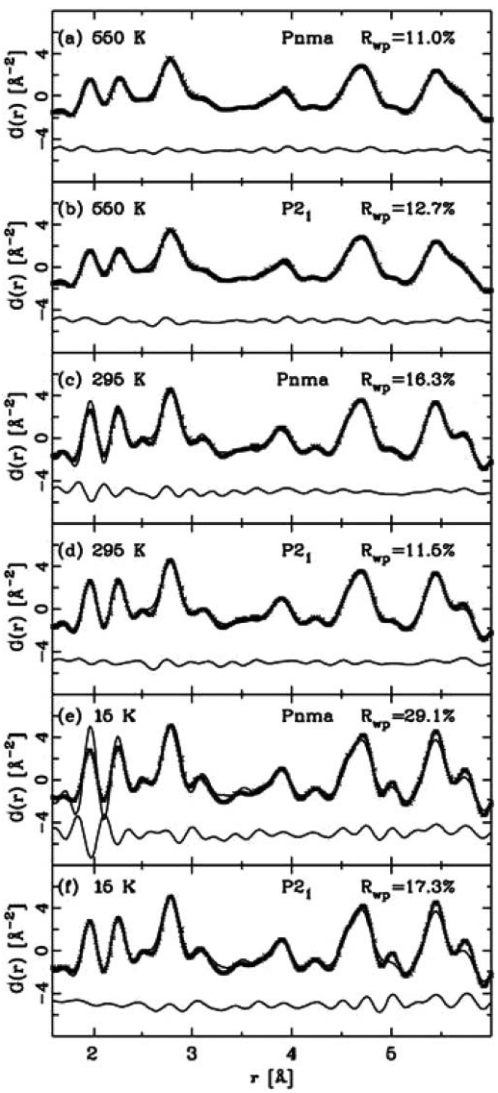


**Fig. 9** PDF refinements over the $r_{min}$ = 1.6 to $r_{max}$ = 6 Å range for $YCrO_3$ in the paraelectric region (550 K) [(a) and (b)] and ferroelectric region (295 and 15 K) [(c)–(f)]. PDF refinements indicate that, in the paraelectric regime, the *Pnma* model is in better agreement with experimental data compared to $P2_1$ while, in the ferroelectric regime, the $P2_1$ model shows better agreement (295 and 15 K). The space group modeled and the corresponding $R_{wp}$ value are indicated. The differences between observed and calculated data are shown below each graph (from ref. 48).

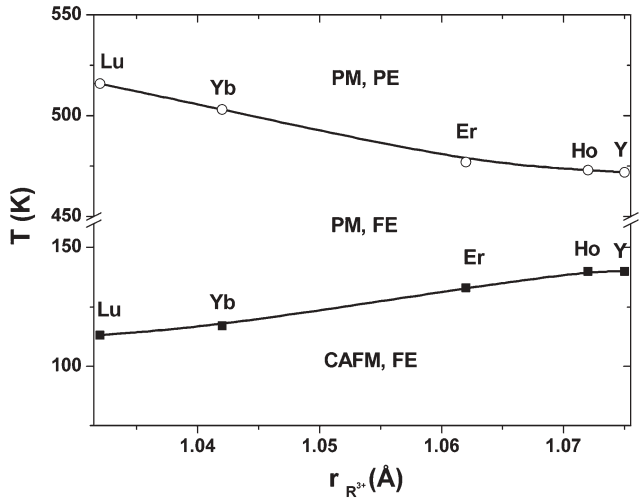


**Fig. 10** Phase diagram of heavy rare earth chromites (from ref. 49).

manganites. It is likely that grain boundaries between the different electronic phases have a role in determining the dielectric behaviour. The importance of grain boundaries in giving rise to high dielectric constants has indeed been recognized.[57,58] In spite of the complexity of their electronic structure, the present study shows that the charge-ordered rare earth manganites possess multiferroic and magnetoelectric properties. Clearly, charge-ordering provides a novel route to multiferroic properties specially in the case of the manganites.

Besides the manganites, $LuFe_2O_4$ which is a charge-ordered bilayer system exhibits electric polarization at the ferrimagnetic transition temperature.[59,60] In addition to $LuFe_2O_4$ other heavy rare earth ferrites such as $ErFe_2O_4$, $YbFe_2O_4$ and $YFe_2O_4$ would be expected to show electric polarization at the ferrimagnetic transition temperatures beside the magnetoelectric effect.

## Concluding remarks

Recent research on multiferroic systems gives an optimistic scenario wherein alternative mechanisms bring about magnetic ferroelectricity in a variety of materials. Some of the important mechanisms that have emerged relate to tilting of metal–oxygen polyhedra, spiral magnetic ordering and stereochemical activity of the Bi lone pair. In many of the multiferroic oxides, magnetic frustration appears to give rise to novel magnetic properties which then induce ferroelectricity. The role of local non-centrosymmetry and charge-ordering of mixed valent ions are two new ideas that have come to the fore. It appears that many ferroelectric materials formally possessing centrosymmetric structure may indeed have local non-centrosymmetry. In principle, non-centrosymmetry can also be achieved by making use of strain, defects and other factors. Multiferroics also offer theoretical challenges besides attractive experimental possibilities. In particular, there is considerable scope for investigations of the large family of charge-ordered manganites and related materials. It is likely that a large number of materials in this family are not only multiferroic but also magnetoelectric, considering the known effects of electric and magnetic fields on these materials.

There is every possibility that magnetoelectric effects in the manganites can be exploited technologically in memory devices, recording and other applications. The recent work of Gajek *et al.*[61] on thin films of $La_{0.1}Bi_{0.9}MnO_3$ promises their use in memory devices. For experimental materials scientists, the challenge of discovering materials exhibiting both magnetism and ferroelectricity with coupling between them makes the subject exciting. Some of the important aspects are related to unified theoretical development, study of spectroscopic properties and discovery of monophasic multiferroic materials showing magnetoelectric coupling.

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