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FAST TRACK COMMUNICATION

Magnetic control of large room-temperature polarization

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Abstract

Numerous authors have referred to room-temperature magnetic switching of large electric polarizations as ‘the Holy Grail’ of magnetoelectricity. We report this long-sought effect, obtained using a new physical process of coupling between magnetic and ferroelectric nanoregions. Solid state solutions of PFW [$\text{Pb}(\text{Fe}_{2/3}\text{W}_{1/3})\text{O}_3$] and PZT [$\text{Pb}(\text{Zr}_{0.53}\text{Ti}_{0.47})\text{O}_3$] exhibit some bi-relaxor qualities, with both ferroelectric relaxor characteristics and magnetic relaxor phenomena. Near 20% PFW the ferroelectric relaxor state is nearly unstable at room temperature against long-range ferroelectricity. Here we report magnetic switching between the normal ferroelectric state and a magnetically quenched ferroelectric state that resembles relaxors. This gives both a new room-temperature, single-phase, multiferroic magnetoelectric, $(\text{PbFe}_{0.67}\text{W}_{0.33}\text{O}_3)_{0.2}(\text{PbZr}_{0.53}\text{Ti}_{0.47}\text{O}_3)_{0.8}$ (‘0.2PFW/0.8PZT’), with polarization, loss (<1%), and resistivity (typically 10^8 – 10^9 Ω cm) equal to or superior to those of BiFeO_3 , and also a new and very large magnetoelectric effect: switching not from $+P_r$ to $-P_r$ with applied H , but from P_r to zero with applied H of less than a tesla. This switching of the polarization occurs not because of a conventional magnetically induced phase transition, but because of dynamic effects: increasing H lengthens the relaxation time by $500\times$ from <200 ns to >100 μs , and it strongly couples the polarization relaxation and spin relaxations. The diverging polarization relaxation time accurately fits a modified Vogel–Fulcher equation in which the freezing temperature T_f is replaced by a critical freezing field H_f that is 0.92 ± 0.07 T. This field dependence and the critical field H_c are derived analytically from the spherical random bond random field model with no adjustable parameters and an E^2H^2 coupling. This device permits three-state logic ($+P_r$, 0, $-P_r$) and a condenser with >5000% magnetic field change in its capacitance; for $H = 0$ the coercive voltage is 1.4 V across 300 nm for $+P_r$ to $-P_r$ switching, and the coercive magnetic field is 0.5 T for $+P_r$ to zero switching.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

At the end of the 19th century, magnetoelectric effects—the manipulation of magnetization by electric field and

induction of polarization by magnetic field—were suggested by Curie [1]. In 1957–9 these suggestions were proved for Cr_2O_3 theoretically by Dzyaloshinskii [2], and experimentally by Astrov [3] in Moscow and by Rado in the USA [4]. And afterwards in the 1970s careful studies were carried out by many groups [5–7] on various magnetoelectric

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materials. In the last decade related studies on ferroelectrics that are weakly magnetic [8–11] and magnets that are weakly ferroelectric [12–14] have been done in order to get novel magnetoelectric materials. As far as we know, there are few single-phase materials in nature that possess both ferroelectric and ferromagnetic properties independently [15]. Magnetoelectric multiferroics are at present defined as single-phase materials [5–11] or artificially designed nanostructures [16, 17] where different ferroic orders such as (anti)ferroelectricity, (anti)ferromagnetism, and ferroelasticity coexist and at least one magnetic and one electric order parameters are coupled with each other. After the fabrication of epitaxial thin films of BiFeO₃ (BFO) with room-temperature multiferroic behavior ($P_r \sim 55 \mu\text{C cm}^{-2}$ @15 kHz, $M_s \sim 1 \text{ emu cm}^{-3}$) [18, 19], much multiferroics research has centered around this material; yet it is well known that BFO is not an ideal magnetoelectric: it often shows very high leakage current and applied H does not much affect polarization P [20, 21]; its bandgap at 2.7 eV is nearly a 1 eV less than that of the present material, and it is a poor ferromagnet.

2. Switching

Recently there has been a serious research effort in many countries to produce electric switching of magnetizations or magnetic switching of polarizations in multiferroic magnetoelectrics. Generally schemes for switching from $+M$ to $-M$ with electric field E have been examined, or conversely from $+P_r$ to $-P_r$ with magnetic field H . BiFeO₃ has been the material of choice at room temperature, but in addition over the past several years a useful hint to the materials design of multiferroics has been obtained by the studies on other magnetic ferroelectrics, including manganites. The rare-earth manganite RMnO₃ (R = Tb, Dy) have shown strong magnetoelectric (ME) properties near the magnetic transitions [8, 9, 22]. Unfortunately these groups of materials show magnetic behavior only at cryogenic temperatures (<50 K). There are several other magnetically frustrated systems that have been identified which also showed gigantic magnetoelectric effects at low temperature. Among these materials MnWO₄ showed strong temperature and external magnetic field dependent of its ferroelectric loops [23, 24]. Similarly, high-temperature multiferroic behavior has been studied in PbFe_{0.5}Ti_{0.5}O₃ [25, 26] and in PbFe_{2/3}W_{1/3}O₃/PbTiO₃ [27, 28]. These results [25, 26] and those of [27, 28] are of particular interest because they showed similar behavior to that in the present investigation.

In the present scenario a new single-phase material is needed that can exhibit magnetoelectricity (not necessarily linear) at room temperature. In search of such new magnetoelectrics we have taken a different approach: ignore subtleties of symmetry and examine multirelaxors in which strong E^2H^2 coupling exists independent of long-range symmetry. In our prior investigation, single-phase Pb(Fe_{0.66}W_{0.33})O₃ (PFW)-PbTiO₃ (20:80) solid solution showed multiferroic relaxor behavior near room temperature with very low dielectric loss [27]. Smolenskii *et al* discovered

various related multiferroics compounds in late 1950s, among which pure PFW is one of the most promising candidates, having a ferroelectric relaxor transition near 180 K and an antiferromagnetic (AFM) phase transition (343 K) above room temperature [29]. Relaxors are materials [30] with short-range polarization ordering and highly frequency dependent dielectric properties. Originally thought by Smolenskii to exhibit inhomogeneously broadened phase transitions, their behavior is in fact very complex and is both defined carefully and reviewed in detail by Samara [31]. Since lead zirconate titanate PbZr_xTi_{1-x}O₃ (PZT) thin films have been extensively studied for potential and practical applications in dynamic and non-volatile ferroelectric random access memories due to their large remanent polarization (P_r), small coercive field and Curie temperature above room temperature [32, 33], it therefore seemed useful in order to exploit the basic properties of these two materials to make a complex single-phase material using a chemical solution technique (CSD). We have carefully examined the properties of PFW/PZT for 20%, 30%, and 40% PFW. All of these samples are weakly ferromagnetic and ferroelectric at some temperature, but increasing amounts of PZT raise the relaxor-to-ferroelectric phase transition from about 150 K at 60% to 300 K at 80%, so that only the 80% PZT specimens combine the most interesting properties at ambient temperatures. A careful study on three naturally occurring multiferroics PFW [27, 28] Pb(Fe_{0.50}Nb_{0.50})O₃, (PFN) [34, 35], and Pb(Fe_{0.50}Ta_{0.50})O₃ (PFT) [35] with the ‘universal’ ferroelectric PZT added has been carried out, since these three multiferroics by themselves are not good enough to provide both good resistivity, multiferroicity, and magnetoelectric coupling. Note that it is not necessary that the materials studied be ferromagnetic at room temperature, since the coupling we see, although very large, is of form E^2H^2 . The magnetic hysteresis loops $M(H)$ of samples with 20% PFW, 30% PFW, and 40% PFW all show weak ferromagnetism at room temperature, with magnetization M from 0.5 to 4.5 emu cm⁻³ with increasing Fe concentration and a low coercive field of approximately 0.12 T. A superexchange in the disordered regions through Fe⁺³-O-Fe⁺³ is expected to yield antiferromagnetic ordering [27, 36] but at the low Fe concentrations in this material weak ferromagnetism is probably caused by spin clustering.

3. Methods

Ferroelectric ‘0.2PFW/0.8PZT’ thin films were deposited on Pt/Ti/SiO₂/Si(100) substrates using both chemical solution deposition (CSD) and pulsed laser deposition. Details are given elsewhere. DC sputtering was carried out for depositing the Pt top electrode of $3.1 \times 10^{-4} \text{ cm}^2$ area using a shadow mask. The dielectric properties in the frequency range of 100 Hz to 1 MHz were studied using an impedance analyzer HP4294A (from Agilent Technology Inc.) over a wide range of temperature attached to a temperature controlled probe station (MMR Technology). Magnetic properties were investigated using a vibrating sample magnetometer (VSM) (Lakeshore model 7400).

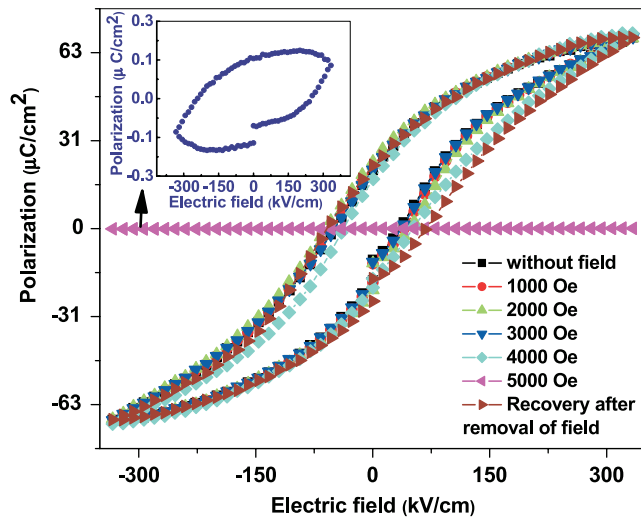


Figure 1. Three-state logic switching ($+P_r$, 0 , $-P_r$) in 0.2PFW/0.8PZT: P - E hysteresis under the application of external magnetic field from 0 to 0.5 T changes polarization from $|P_r|$ to zero; application of 1.4 V across 300 nm changes $+P_r$ to $-P_r$. The inset is the $P = 0$ relaxor state on expanded scale, showing a linear lossy dielectric. Note that the polarization values assume that the gold electrodes do not diffuse under the masks; due to such diffusion the real values of P may be only about half the graphed values.

4. Structure and XRD

X-ray diffraction patterns (XRD) were obtained of the ‘0.2PFW/0.8PZT’ thin films deposited on Pt/TiO₂/SiO₂/Si substrates at 400 °C and post-annealed from 600 to 750 °C for different rapid thermal annealing (RTA) time. As-grown films are amorphous in nature. The XRD analysis indicates that the films grown at 700 °C were single-phase polycrystalline in nature with less than 0.1% impurities (pyrochlore) phases. A preliminary XRD investigation was carried out with the well-known POWD program [37] which fitted well a tetragonal crystal structure having lattice parameters $a = 4.0217$ Å and $c = 4.0525$ (standard deviation each of 0.0060). The intensity of the (100), and (110) peaks of ‘0.2PFW/0.8PZT’ films increases with an increase in temperature, illustrating a better crystalline state and enhancement in grain size. The observed bigger grain size and higher surface roughness may be due to growth at high temperature and utilization of the conventional chemical solution deposition process [20].

5. Dielectric properties

The dielectric constant and dielectric loss show a broad dielectric dispersion from 100 Hz to 1 MHz over a wide range of temperature for higher frequency.

The electric field induced polarization switching (P - E) behavior was studied by Sawyer-Tower measurements at 60 Hz. The films exhibit well saturated hysteresis loops with remanent polarization (P_r) and the coercive field (E_c) of about $22 \mu\text{C cm}^{-2}$ and 48 kV cm^{-1} (1.4 V across 300 nm) respectively for 350 kV cm^{-1} maximum external electric field. We did not observe much change in the coercive field with

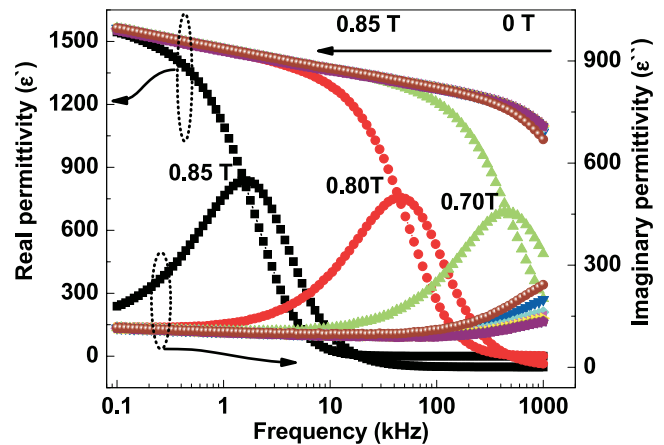


Figure 2. The real and imaginary part of dielectric permittivity (arrows show the direction of the real and imaginary part) as a function of frequencies under the application of external magnetic field from 0 to 0.85 T.

an increase in applied electrical field. The observed P_r value is at par with the reported value of polycrystalline PZT thin films annealed at 650 °C [38]. The samples exhibited little fatigue. Twelve per cent decay in fatigue of ‘0.2PFW/0.8PZT’ thin films on a platinumized silicon substrate after 10^9 cycles is much better than the earlier reports for PZT [39], indicating its suitability for memory device applications.

6. Three-state logic ($+P_r$, 0 , $-P_r$)

Three-state logic and switching at room temperature is shown in figure 1. $+P_r$ to $-P_r$ switching is observed at $E_c = 48 \text{ kV cm}^{-1}$ (1.4 V across 300 nm); and magnetic switching from $+P_r$ to zero is shown at 0.5 T. In microelectronics memory applications, as discussed by one of us in numerous publications, it is of greater interest to switch magnetization M with electric field E than to switch polarization P with magnetic field H . (An electric write operation combined with magnetic read is optimum.) However, as Kimura *et al* [8] has shown, switching P with H is of considerable academic interest also, and Karmarkar and Viehland *et al* [40] have emphasized this use for detectors. We note here that the switching requires 0.5 T, a rather large field; however, the device can be placed in a dc field of $H = 0.49$ T with then only 100 G required to switch. Three-state logic at a switching field of 100 G might be very useful. The effect we report is not ‘persistent’ in the sense used by Eerenstein *et al* [14]; that is, the magnetic field must be left on, not pulsed. In this sense the light switch in your bedroom is also not persistent; it must be left in the up position to stay on.

The polarization response at 0.5 T is shown in the inset in figure 1; it is that of a leaky linear dielectric. The reason for this behavior is shown clearly in figure 2, where we have graphed the dielectric constant versus frequency at different magnetic fields. Note that, for example, the dielectric constant at $H = 0.80$ T is 1430 for $f = 1$ kHz but 233 at $f = 100$ kHz. This is simply due to the field dependence of the relaxation time, and the fact that as H increases the

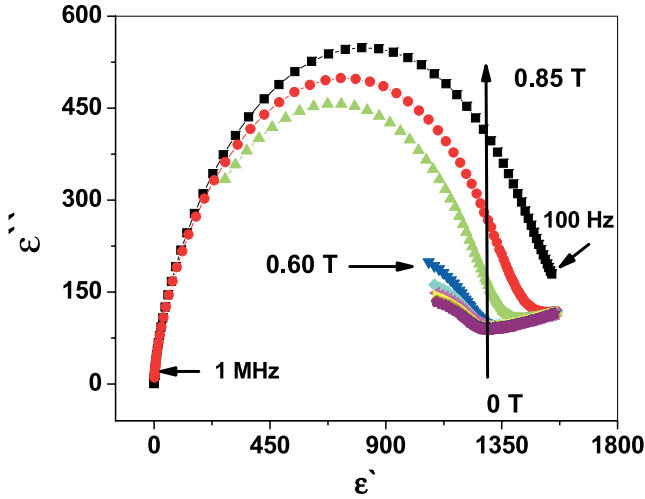


Figure 3. Cole–Cole plot of dielectric data under the action of applied magnetic field, it stretched exponential parameters are used to calculate the relaxation time.

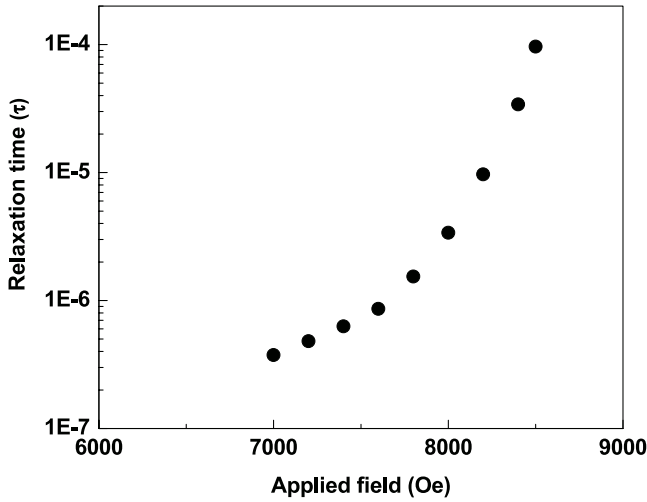


Figure 4. Relaxation time as a function of applied magnetic field.

size (correlation length) of spin clusters in this magnetic relaxor increases and hence their fluctuation time decreases (in an extrapolated infinite field H , the system would have long-range ferromagnetic order and the relaxation frequency would go to zero). The fact that this strongly influences their dielectric susceptibility requires strong coupling between spin fluctuations and polarization fluctuations. In a separate paper we relate these observations to the recent discovery of multiferroic relaxors by Levstik *et al* [41] and peripherally to the model of magnetic relaxor/ferroelectric relaxor coupling of Shvartsman *et al* [42]. In the theory section below we show that these results can be derived analytically from the spherical random bond random field (SRBRF) model and that the key term is biquadratic E^2H^2 . Figure 2 shows that the peak of the dielectric loss at $H = 0.85$ T is at $f = \text{ca } 2\text{--}3$ kHz. Note that this agrees with the inflection frequency of 2–3 kHz estimated from real part of permittivity figure 2, suggesting a magnetic field induced Debye relaxation.

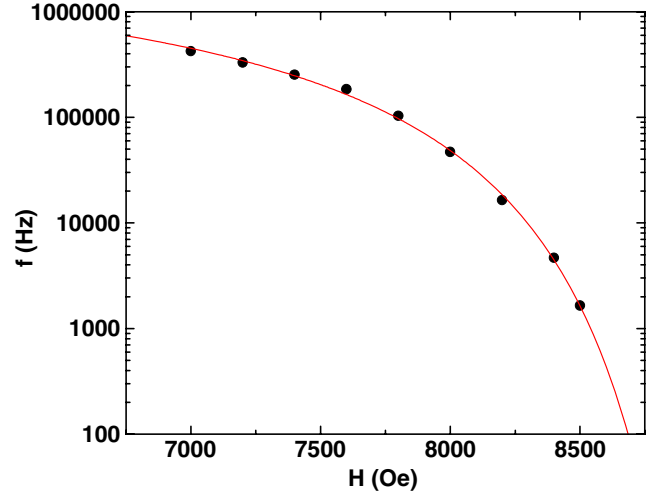


Figure 5. Vogel–Fulcher-type fitting of relaxation frequency; the solid curve is a least square fit to equations (1a).

The relaxation time obtained from the characteristic peak in dielectric loss spectra from figure 2 and/or from the stretched exponential parameters of figure 3 are plotted in figure 4. It indicates that increasing H lengthens the relaxation time by 500× from <200 ns to >100 μs, and it couples strongly the polarization relaxation and spin relaxations. These characteristic frequencies can be accurately fitted to high precision the Vogel–Fulcher-type equation:

$$f = f_0 \exp\left(-\frac{U_2}{H_f^2 - H_R^2}\right) \quad (1a)$$

where H_f is a freezing field and replaces the analogous term in T_f (freezing temperature) in the usual Vogel–Fulcher equation; μ_B is the Bohr magneton; and H_R , the relaxation field. Equation (1a) arises from an E^2H^2 term in the free energy and is independent of the sign of H . The fitted data provide freezing field $H_f = 0.92 \pm 0.07$ T and characteristic frequency $f_0 = 40 \pm 1$ MHz as shown in figure 5. Although the diverging polarization relaxation time also fits the modified Vogel–Fulcher equation in equation (1b),

$$f = f_0 \exp\left[\frac{-E_a}{\mu_B(H_f - H_R)}\right] \quad (1b)$$

this equation would arise from an E^2H term in the free energy which can be ruled out by the independence of the polarization data upon the sign of applied field H . The coupling of order parameters in relaxors is addressed in [43, 44] and is detailed below, using the spherical random bond random field model. The coupling constant is taken as real; the general description of coupled oscillators permits either real or imaginary coupling, with the latter implying decay into the same final state [45]. Tokunaga *et al* reported for $\text{Dy}_x\text{Bi}_{1-x}\text{FeO}_3$ that if the applied magnetic field (H) is greater or equal to the reorientation of Fe spins (H_{re}^{Fe}), it produces a weak ferromagnetic component along the c -axis of the crystal and is able to generate or ‘flop’ the ferroelectric polarization [22] from P_r to zero (similar to a magnetic spin

flop). That is a kind of magnetic phase transition. But what we invoke in the present case is somewhat more complex and not strictly a phase transition at all, because like conventional relaxors, it is frequency dependent; it is the decrease in relaxation time below the measuring probe frequency, brought on by spin alignment and increased spin correlation length in increased external magnetic fields.

7. Theory

We now discuss the origin of the magnetic field modified Vogel–Fulcher (VF) relaxation rate observed in ‘0.2PFW/0.8PZT’. It has been suggested earlier [43] that the basic relaxation mechanism in relaxor ferroelectrics is growth and percolation of polar nanoregions (PNRs). The main assumption is that the local electric field inside the polarization cloud of a PNR falls off with distance as $\sim 1/r^3$. The potential energy of an induced dipole at r is balanced against the thermal fluctuation energy $\sim kT$, thus yielding the correlation volume $v_c \sim 1/T$. The volume fraction of PNRs then grows as $\sim 1/T$ until the percolation limit T_p is reached, corresponding to the VF temperature T_0 .

The local electric field in a PNR in the presence of magnetoelectric (ME) coupling will be derived from the Landau-type free energy of a multiferroic system

$$F_0(P, M) = \frac{1}{2}\chi_{m,i}^{-1}P_i^2 + \frac{1}{2}\chi_{m,j}^{-1}M_j^2 + \frac{1}{4}b_e P^4 + \frac{1}{4}b_m M^4 + \dots - E_i P_i - H_j M_j. \quad (2)$$

The dielectric susceptibility tensor is diagonal, $\chi_{e,ij} = \delta_{ij}\chi_{e,i}$, representing the response of a disordered ferroelectric close to the boundary between the ferroelectric and relaxor phase. An explicit expression for $\chi_{e,i}$ can be obtained from the SRBRF model of relaxor ferroelectrics [44]. Similarly, the magnetic susceptibility $\chi_{m,j}$ for a weakly ferromagnetic subsystem is defined in S.I. units⁵ as $M_i = \chi_{m,ij}H_j$. The anharmonic coefficients b_e, b_m formally ensure thermodynamic stability. No direct ME coupling terms appear in equation (2) since experimental evidence of them is missing. However, an indirect ME effect [14] will be induced via electrostrictive and magnetostrictive strains, $u_k = Q_{e,ki}P_i^2$ and $u_l = Q_{m,jl}M_j^2$, with electro and magnetostriction coefficients $Q_{e,ki}$ and $Q_{m,lj}$, respectively. These are related to the inverse susceptibility tensors by the Maxwell relations $Q_{ki} = -(1/2)(\partial\chi_i^{-1}/\partial X_k)_T$, where the stresses X_k are related to strains through the elastic constants $X_k = C_{kl}u_l$. The Voigt notation and summation convention are implied as appropriate.

Expanding the inverse susceptibilities in equation (2) to linear order in X_k , applying the Maxwell relations, and adding the elastic energy $(1/2)C_{kl}^{-1}X_k X_l$, we obtain after minimizing the free energy a new fourth-order ME term

$$F_1(P, M) = -\frac{1}{2}\lambda_{ij}P_i^2 M_j^2, \quad (3)$$

where the ME coupling coefficient is $\lambda_{ij} = 2C_{kl}Q_{e,ki}Q_{m,lj}$.

The equilibrium condition $\partial(F_0 + F_1)/\partial P_i = 0$ yields the electric field $E_i = \chi_{e,i}^{-1}P_i(1 - \chi_{e,i}\lambda_{ij}M_j^2)$ to linear order in P .

⁵ By definition, $\chi_{e,i} = \varepsilon_0(\varepsilon_i - 1)$ and $\chi_{m,j} = \mu_0(\mu_j - 1)$ thus M is in Tesla (Kennelly convention); for details see [46].

It immediately follows that the local electric field within each PNR similarly acquires an additional contribution proportional to $M_j^2 = \chi_{m,j}^2 H_j^2$. This contribution now appears at each step in the derivation of the VF equation [43].

For any direction of H_j all orientations of PNR polarizations P_i are allowed. Moreover, in view of random isotropy the average volume fraction of PNRs is independent of the direction of H . Performing a linear average of λ_{ij} over i and j , and introducing hydrostatic coefficients $Q_h = Q_{11} + Q_{12} + Q_{13}$ we obtain the averaged coupling constant $\bar{\lambda} = 2C_h Q_{e,h} Q_{m,h}$, where $C_h = \frac{1}{9}\sum_{kl=1}^3 C_{kl}$ is the bulk modulus.

The VF temperature T_0 thus becomes a field dependent quantity $T_0(H) = T_0(1 - \chi_e \chi_m^2 \bar{\lambda} H^2)$. The VF relaxation time diverges on the line of percolation critical points $T = T_0(H)$ in the T, H plane. The sign of $\bar{\lambda}$ is determined by the signs of $Q_{e,h}$ and $Q_{m,h}$, which can be either positive or negative. If $\bar{\lambda} < 0$, the PNRs will freeze at a VF temperature higher than its zero-field value T_0 . This seems to be the case in ‘0.2PFW/0.8PZT’. The VF relaxation rate at fixed temperature can be written as a function of the magnetic field

$$f = f_0 \exp\left(-\frac{U_2}{H_f^2 - H^2}\right), \quad \text{for } H < H_f \quad (4)$$

in agreement with the empirical result equation (1a). The barrier height $U_2 = H_0^2 U/kT_0$ is given in terms of the zero-field VF parameters U/kT_0 and a scaling field $H_0^2 = 1/(\chi_e \chi_m^2 |\bar{\lambda}|)$. The critical field is given by $H_f^2 = H_0^2(T - T_0)/T_0$ or

$$H_f^2 = \frac{T - T_0}{T_0} \frac{1}{2\chi_e \chi_m^2 C_h |Q_{e,h} Q_{m,h}|}. \quad (5)$$

Thus H_c can be expressed in terms of independently measurable physical parameters of the system.

Although the parameters occurring in this expression are generally unknown for ‘0.2PFW/0.8PZT’, using averages of known values of electrostriction and magnetostriction in the quasi-isotropic approximation $Q_{\text{eff}} = Q_{11} + 2Q_{12}$ for other perovskite oxides [47] yields an estimate of $H_f^2 = 0.3 \pm 0.2 \text{ T}^2$, i.e., $H_f = 0.5 \pm 0.2 \text{ T}$, giving factor of two agreement with the experimental $H_f = 0.92 \text{ T}$. Our theory does not yield the sign of the coupling constant $\bar{\lambda}$, which experimentally is negative (applied H turns ferroelectricity into relaxor behavior). Electrostrictive and magnetostrictive tensor components in perovskite oxides are typically of the same magnitude but vary in sign; therefore until one measures them individually we cannot definitively calculate the sign. Alternative models: it might also be possible that the magnetic behavior of electric polarization $P(H)$ arises from some more pedestrian cause, such as the change in coercive field E_c with magnetic field. In this case the polarization P might remain unchanged with field H but be unable to switch due to increases in E_c . However, such a model cannot readily explain either the dependence of dielectric constant $\varepsilon(H)$ or the relaxation time $\tau(H)$ shown here.

Table 1. Characteristics of lead iron tungstate–lead zirconate titanate solid solutions.

Characteristic	20%PFW/80%PZT	30%PFW/70%PZT	40%PFW/60%PZT
Structure and lattice constants (nm)	Tetragonal $a = 0.4022 \pm 0.0006$ $c = 0.4053 \pm 0.0006$	Cubic $a = 0.4012 \pm 0.0003$	Cubic $a = 0.4007 \pm 0.003$
Electrical polarization	$P_r = 22 \mu\text{C cm}^{-2}$ at 295 K	$P_r = 20 \mu\text{C cm}^{-2}$ at 200 K	$P_r = 11 \mu\text{C cm}^{-2}$ at 150 K
Magnetization	$M_r = 0.48 \text{ emu cm}^{-3}$ at 295 K	$M_r = 2.29 \text{ emu cm}^{-3}$ at 295 K	$M_r = 4.53 \text{ emu cm}^{-3}$ at 295 K
Dielectric diffusiveness coefficient γ	1.78 ± 0.05 (intermediate ferroelectric/relaxor)	2.00 ± 0.10 relaxor	2.00 ± 0.05 relaxor
Dielectric constant ϵ (295 K)	1380	1020	720
Dielectric loss δ (295 K)	0.003	0.02	0.06

8. Summary

In conclusion, this manuscript reports the successful synthesis of a novel single-phase complex perovskite room-temperature magnetoelectric multiferroic. A narrow temperature window was found to get the desired phase. High dielectric constant, low dielectric loss, highly frequency-dispersive susceptibility, more than 50% temperature dependent dielectric tunability, and above-room-temperature dielectric maxima were observed in ‘0.2PFW/0.8PZT’ thin films. They show a ferroelectric polarization of $22 \mu\text{C cm}^{-2}$ and low coercive field of 48 kV cm^{-1} with 12% fatigue in polarization after 10^9 cycles, thus suggesting a potential candidate for memory applications. At room temperature a weak ferromagnetic/antiferromagnetic M – H hysteresis was detected which suggests an extra degree of freedom of Fe ions in complex octahedra, tilting of Fe^{+3} –O– Fe^{+3} linkage, and charge ordering with nearest neighbors. The ferroelectric hysteresis flops under the application of external magnetic field ($>0.50 \text{ T}$), revealing a strong magnetoelectric coupling in the present system, but this is not direct—rather it is indirect through strain via electrostriction plus magnetostriction. It is not due to a conventional magnetically induced phase transition (instead, due to a field dependent spin relaxation time). This new magnetoelectric effect, switching from $+P_r$ to zero with applied magnetic field, is $1000\times$ greater than in rare-earth manganites and occurs at room temperature, suggesting a variety of new magnetoelectric devices, including very large magneto-capacitance and three-state logic elements [48]⁶. This effect is not limited to the 20:80 PFW/PZT compound; table 1 gives data for 30:70 and 40:60 ratios. However since these compounds have their interesting properties below room temperature, they are of less device interest (the physics, however, is exactly the same). In table 1 the diffusiveness coefficient g is the exponent in the dependence of dielectric constant versus reduced temperature $\epsilon(T) = C(T - T_c)^g$ near the Curie temperature; for ferroelectrics it is 1, and for classical relaxors it is 2.

⁶ Three-state switching using magnetic fields plus resistive switching has been reported by [49].

Acknowledgments

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