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Room-temperature single phase multiferroic magnetoelectrics: Pb(Fe, M)x(Zr,Ti)(1-x)O3 [M = Ta, Nb]

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We describe extensive studies on a family of perovskite oxides that are ferroelectric and ferromagnetic at ambient temperatures. The data include x-ray diffraction, Raman spectroscopy, measurements of ferroelectric and magnetic hysteresis, dielectric constants, Curie temperatures, electron microscopy (both scanning electron microscope and transmission electron microscopy (TEM)) studies, and both longitudinal and transverse magnetoelectric constants with Fe concentrations, supporting the earlier conclusions of a key role for Fe spin clustering. The room-temperature orthorhombic C2v point group symmetry inferred from earlier x-ray diffraction studies is confirmed via TEM, and the primitive unit cell size is found to be the basic perovskite Z = 1 structure of BaTiO3, also the sequence of phase transitions with increasing temperature from rhombohedral to orthorhombic to tetragonal to cubic mimics barium titanate. © 2013 American Institute of Physics. [http://dx.doi.org/10.1063/1.4790317]

I. INTRODUCTION

It has been known for several years1–6 that the perovskite oxides PbFe1/2Ta1/2O3 (PFT), PbFe1/2Nb1/2O3 (PFN), and PbFe2/3W1/3O3 (PFW) are multiferroics with long-range magnetic ordering near or above room temperature. Our earlier studies showed7–17 that solid solutions of these materials with PbZrxTi1-xO3 and pure PbTiO3 yielded single-phase ferroelectric crystals whose weak ferromagnetism persists to room temperature or above. The low electrical conductivity of these materials thus produced a good alternative to BiFeO3 for commercial device materials with intended embodiments as multi-magnetic tunnel junctions23–25 or THz generators.26–28

Of the members of this family of quaternary B-site perovskites, the Fe/W/Zr/Ti compounds exhibit only biquadratic coupling between polarization (P) and magnetization (M), and not linear magnetoelectricity. However, the remarkable dependence of electrically switched polarization P upon dc magnetic field H (vanishing above H = 0.9 T) due to magnetically dependent relaxation times29 may still permit some practical devices. By comparison, the single-phase compounds with Fe/Ta/Zr/Ti or Fe/Nb/Zr/Ti at the B-site are linear magnetoelectrics at room temperature, with bilinear coupling in their free energy of form G(P,M,T) = α(T)PiMj. These materials are emphasized in the present report.

Semantics: since Fe spin clustering plays a key role in the room-temperature magnetoelectricity of these materials, it is useful to ask whether they may be considered to be nanocomposites rather than single-phase crystals. This is more a question of terminology than of physics, but usually composite designates a material with two or more well-defined substances, and a non-random distribution of B-site ions does not constitute two phases, nano-phases or otherwise. A few investigators30 have asked whether these new materials are different from BaTiO3 doped with Fe. Our answer is yes, because iron-doped barium titanate certainly has both magnetic and ferroelectric properties, but the magnetism is that of paramagnetic isolated impurities. If BaTiO3 were heavily doped (several percent or more), it would be a new material and might have magnetoelectric properties; but it would be necessary to demonstrate that it is single-phase and that the Fe ions exhibit significant exchange coupling. We emphasize that single-phase materials need not have all ions perfectly ordered; there are many families of ferroelectrics that are disordered, some of which are relaxors.

II. EXPERIMENTAL

A. Sample preparation

Ceramic samples of Pb(Fe0.5Nb0.5)x(Zr0.53Ti0.47)1-xO3 (PFNx-PZT(1-x)) and Pb(Fe0.5Ta0.5)y(Zr0.53Ti0.47)1-yO3 (PFTy-PZT(1-y)) were prepared by a conventional solid state reaction route. Analytical-purity oxides, PbO, ZrO2, TiO2,
Fe$_2$O$_3$, Ta$_2$O$_5$, and Nb$_2$O$_5$ (Alfa Aesar) with purity of 2-3 nines, were used as raw materials. The powders of the respective metal oxides were mixed in a planetary high-energy ball mill with tungsten carbide media and then were calcined at 850 °C for 10h in a closed alumina crucible. 10% excess of PbO was added to each composition to compensate Pb deficiency during the high temperature processing. Poly (vinyl alcohol) solutions (1%) were added to the calcined powders as a binder. The dried powders were granulated by passing them through a 150 μm-mesh sieve and pressed using a hydrostatic press (3.5 × 10^8 Pa) into pellets of 10 mm diameter. The pressed pellets were heat treated at 600 °C for the removal of organic binders followed by sintering at 1100–1250 °C for 4h. All heat treatments were performed in air. In order to prevent the PbO loss during high temperature sintering and to maintain desired stoichiometric, an equilibrium PbO vapor pressure was established with PbZrO$_3$ as setter by placing pellets in a covered alumina crucible. The flat polished surfaces of the sintered pellets were electroded with high purity silver paint and then dried at 200 °C before making electrical measurements.

B. Characterization techniques

Orientation and phase purity of the powders and sintered pellets were determined by x-ray diffraction (XRD) (Siemens D5000) using CuK$_\alpha$ radiation with wavelength of $\lambda = 1.5405$ Å. Raman measurements were performed in the backscattering geometry using the 514.5 nm line from an Ar laser. The scattered light was dispersed by T64000 spectrometer and collected with a charge-coupled device (CCD) detector. Ferroelectric hysteresis loops were measured at room temperature using a hysteresis loop tester (Radiant Technologies RT6000 HVS) at 50 Hz in a voltage range from 800 V to 1800 V. Magnetic measurements were carried out using a vibrating sample magnetometer (VSM). Dielectric measurements (capacitance and loss factor) were carried out in the temperature range of 100 to 700 °C for frequencies between 100 Hz and 1 MHz by using a programmable temperature controller (MMR K-20) and an impedance analyzer (HP 4294A). Field emission scanning electron microscope (FESEM: JEOL JSM-7500F) and a scanning transmission electron microscopy (STEM) equipped with energy dispersive X-ray spectroscopy (EDX) was used to observe the chemical composition of the ceramic samples. The magnetoelectric voltage coefficient for ceramic samples of ~0.5 mm and poled in a constant electric field of 2.4 V/m (applied voltage = 1200 V) for 12 h was determined by dynamic methods as a function of bias field H at ac field $H_{ac} = 0.5$ Oe and frequency 1 kHz by measuring the voltage across the samples utilizing a lock-in-amplifier.

III. DISCUSSION

A. X-ray results: Structure and symmetry

Figure 1(a) shows the x-ray diffraction patterns for Pb(Fe$_{0.5}$Nb$_{0.5}$)$_x$(Zr$_{0.53}$Ti$_{0.47}$)$_{1-x}$O$_3$ (PFN$_x$-PZT$_{(1-x)}$) (0.1 ≤ x ≤ 0.4) ceramic samples. These results reveal single phase perovskite structure without the appearance of any secondary phase (e.g., pyrochlore). The diffraction patterns were indexed, according to previously reported results for tetragonal PbZr$_{0.55}$Ti$_{0.45}$O$_3$ (PZT). This is an excellent result considering that the center of the perovskite octahedra could be occupied randomly by Nb$^{5+}$, Fe$^{3+}$, Zr$^{4+}$, or Ti$^{4+}$, which makes it difficult to obtain pure perovskite phase. Figures 1(b)–1(e) show a close view of the evolution of (101) and (200) peaks of PFN$_x$-PZT$_{(1-x)}$ and (PFT$_y$-PZT$_{(1-y)}$) with x or y concentration, respectively. With the increase of PFN(x) or PFT(y) contents there is a systematic shift in the peak positions toward the higher diffraction angle (2θ) that could be due to substitution of ions with smaller ionic radii, in this case Zr$^{4+}$ (0.72 Å) and Ti$^{4+}$ (0.605 Å) by Ta$^{5+}$, Nb$^{5+}$ (0.64 Å), and Fe$^{3+}$ (0.67 Å). With the increase of x/y concentrations the peaks associated with (200) reflection become wider, and a clear splitting for PFN$_x$-PZT$_{(1-x)}$ was seen for x = 0.4, while a narrow but asymmetrical peak was observed for the same composition for PFT$_y$-PZT$_{(1-y)}$. The temperature dependent XRD studies on PFT$_y$-PZT$_{(1-y)}$ for y = 0.3 and 0.4 showed an orthorhombic structure for these solid solutions at ambient temperature, but this is not obvious for smaller PFT concentrations y.

B. Raman spectroscopy

The room-temperature Raman spectra of PZT and PFN$_x$-PZT$_{(1-x)}$ (x = 0.1-0.4) are shown in Fig. 2. The Raman
spectrum of ceramic PZT contains a series of broad overlapping bands, which is typical of samples with tetragonal phase in this composition range.31 According to the factor group analysis the tetragonal PZT has 12 optical normal modes of symmetry $C = 4E + 3A_1 + B_1$ that are Raman modes.32 Raman spectra of PZT showed the low frequency phonon modes E(TO$_1$) and E(LO$_1$) at ~90 cm$^{-1}$ and ~132 cm$^{-1}$; four additional peaks appeared at 224 cm$^{-1}$, 275 cm$^{-1}$, 565 cm$^{-1}$, and 740 cm$^{-1}$.33 Raman spectra of PFN-PZT show a pseudo-tetragonal structure at room temperature for most concentration ranges, and so we assign these peaks to E(TO$_2$), $B_1 + E$ and $A_1$ (TO$_3$), and $A_1$ (LO) modes, respectively.33 Dilson et al. reported for PFT-PZT ($x = 0.3$ and $x = 0.4$) that temperature dependent Raman and XRD studies revealed these materials are orthorhombic at room temperature. However, the lowest E(TO$_1$) frequency mode is not seen clearly in PFN$_x$PZT$_{1-x}$ spectrum because of strong Rayleigh scattering intensity. The modes E(TO$_2$) and $B_1 + E$ correspond to BO$_6$ rotation, while $A_1$ (TO$_3$) and $A_1$ (LO) are related to O-B-O bending and B-O stretching of the oxygen octahedron, respectively.34

These modes shifted toward the lower frequencies with increase in the PFN contents. The decrease in wavenumber with increasing PFN contents is due to the difference in the atomic mass of Zr (91.22 g) and Ti (47.87 g) when they are replaced by Fe (55 g), and Nb (92.90 g) in the B site. The high frequency phonon mode at ~830 cm$^{-1}$ appearing for $x = 0.1-0.4$ resembles to the $A_{1g}$ phonon mode of PFN at 854 cm$^{-1}$ which is attributed to the vibration of oxygen ions in the oxygen octahedra (Nb-O-Fe stretching mode).35

C. Electrical hysteresis loop (remanent polarization $P_r$ and coercive field $E_c$)

The electric field induced polarization switching ($P$-$E$) behavior was studied at low frequency (50 Hz) utilizing Sawyer-Tower experimental set up. The electrical hysteresis loops for 10%, 20%, 30%, and 40% PFN are shown in Fig. 3(a), the strong ferroelectricity of PFN$_x$PZT$_{1-x}$ was evidenced by well defined and saturated and low loss curves, with a remanent polarization of about 20-30 μC cm$^{-2}$. In general, enhancement in remanent polarization ($P_r$) and coercive field ($E_c$) were observed with increasing $x$, however an increase in the broadened the ferroelectric loop was seen with $x$, maybe due to increase in the conductivity. The evolution of $P_r$ and $E_c$ for PFN$_x$PZT$_{1-x}$ and PFT$_y$PZT$_{1-y}$ as a function of PFN-x and PFT-y concentrations, respectively, are shown in Figure 3(b). With increase of PFT-y concentration from $y = 0.1$ to 0.4 almost insignificant change in $P_r$ (15–17 μC cm$^{-2}$), but $E_c$ change from 10-15 kV cm$^{-1}$, while a significant increase in these quantities was observed with increase in PFN-x, i.e., $P_r$ (17–31 μC cm$^{-2}$) and $E_c$ (17-31 kV cm$^{-1}$). These values are comparable with other studies done in similar systems.36–42

D. Magnetic hysteresis (remanent magnetization $M_r$ and coercive fields $H_c$)

Room temperature magnetization vs applied magnetic field curves of PFN$_x$PZT$_{1-x}$ ceramic are shown in

FIG. 2. Room temperature Raman spectra of PZT and Pb(Fe$_{0.5}$Nb$_{0.5}$)$_x$ (Zr$_{0.53}$Ti$_{0.47}$)$_{1-x}$O$_3$ ($x = 0.1, 0.2, 0.3, 0.4$) ceramics.

FIG. 3. Room temperature (a) Ferroelectric loop for Pb(Fe$_{0.5}$Nb$_{0.5}$)$_x$ (Zr$_{0.53}$Ti$_{0.47}$)$_{1-x}$O$_3$ ($x = 0.1, 0.2, 0.3, 0.4$) ceramics. (b) Remanent polarization ($P_r$) and the respective electric coercive field ($E_c$) for PFN$_x$PZT$_{1-x}$ and PFT$_y$PZT$_{1-y}$ as a function of the concentration (x or y).
Fig. 4(a). Magnetization studies of these materials present well behaved magnetization ($M$) vs. applied magnetic field ($H$) loop at room temperature for PFN-$x$ concentration between 0.1 and 0.4, however an improvement in magnetic properties was observed for $x = 0.2$ and $x = 0.3$, while a notable deterioration of these properties was observed for $x = 0.4$. The remanent magnetization of PFN$_x$-PZT$_{1-x}$ ($0.1 \leq x \leq 0.4$) has a maximum of ca. 0.06 emu g$^{-1}$, this is 7% of the maximum possible value for all Fe spins aligned at $T = 0$ and is gives some estimate of the degree of spin clustering at room temperature, the values obtained are comparables to the values reported by R. Blinc et al. for PFN ceramic multiferroic relaxor.\textsuperscript{43} In Figure 4(b), we compare the remanent magnetization ($M_r$) and coercive magnetic field ($H_c$) obtained from $M$ vs. $H$ curve for PFN$_x$-PZT$_{1-x}$ and PFT$_y$-PZT$_{1-y}$ solid solution ceramic samples with $x$ or $y$ varying between 0.1 and 0.4. Similar trend for $M_r$ and $H_c$ was observed in both families, the higher magnetic properties were observed for $x/y = 0.2$.

E. Dielectric properties (capacitance, loss, and Curie temperatures)

The temperature variation of the dielectric constant ($\varepsilon$) and loss tangent ($\tan \delta$) for PFN$_x$-PZT$_{(1-x)}$ compositions were plotted in Fig. 5(a) at 10 kHz. It was not possible to measure the dielectric permittivity at higher temperature due to our experimental limitations in order to observe the phase transitions in sample with $x = 0.1$. However, we can see the variation of dielectric maximum temperature shifting toward lower temperature with increase in PFN composition. It is well known that the transition temperature ($T_c$) of PZT is $T_c \sim 900$ K,\textsuperscript{40,44} with increase in $x$ content of PFN$_x$-PZT$_{(1-x)}$ significant influence on the ferroelectric-paraelectric phase transition was observed. $T_c$ decreased from $\sim 689$ K, to 585 K with $x$ increasing from 0.2 to 0.4, respectively.

On the other hand, the temperature dependence of loss tangent for PFN$_x$-PZT$_{(1-x)}$ ceramics showed almost the same trend for all compositions with an increase of $\tan \delta$ with temperature, below 500 K. However, above 500 K, the composite samples showed a rapid increase with temperature depending upon the compositions. A noticeable increase in $\tan \delta$ accompanied by frequency dispersion is considered to be normal in ferroelectrics containing iron. The existence of the Fe ion, which is a transition element, may be responsible for the increased ionic conduction, resulting in the increase
in tanδ at higher temperatures. Figure 5(b) shows $T_c$ as a function of x/y concentrations for PFN$_x$-PZT$_{(1-x)}$ and PFT$_y$-PZT$_{(1-y)}$, with increase in x/y contents, a significant influence on ferroelectric phase transition was observed. For PFN$_x$-PZT$_{(1-x)}$ the $T_c$ value decreased from (687 K, $x = 0.2$) to (453 K, $x = 0.8$), while for PFT$_y$-PZT$_{(1-y)}$ the $T_c$ shifted from higher temperature ($\sim 528$ K, $y = 0.3$) to low temperature ($\sim 340$ K, $y = 0.8$). The $T_c$ values for PFN$_x$-PZT$_{(1-x)}$ and PFT$_y$-PZT$_{(1-y)}$ compounds are between ~690 K, $T_c$ for PZT, $x = 0$ and 383 K, $T_c$ for PFN, $x = 1$ or 245 K, $T_c$ for PFT, $y = 1$ (Ref. 45), respectively, (see the horizontal lines in Fig. 5(b)).

F. Transmission electron microscopy and field emission scanning electron microscopy (FESEM)

Field emission scanning electron microscope (FESEM) equipped with EDX by elemental composition mapping to the individual Pb(Fe$_{0.5}$Nb$_{0.5}$)$_x$(Zr$_{0.53}$Ti$_{0.47}$)$_{1-x}$O$_3$ ($x = 0.2$) grain of about 1 μm diameter (Fig. 6(a)) and Pb(Fe$_{0.5}$Ta$_{0.5}$)$_y$(Zr$_{0.53}$Ti$_{0.47}$)$_{1-y}$O$_3$ ($y = 0.4$) lamella cut by focus ion beam from the single grain (Fig. 6(b)). Figs. 6(a) and 6(b)-red square (upper) show the SEM image of the scanning area used to perform the compositional analysis for the respective material. Figure 6(a) (lower) show the elemental mapping results of the PFN$_x$-PZT$_{(1-x)}$ single grain that clearly reveal the presence of the all elements (Pb, Fe, Nb, Zr, Ti, and O) of the compound, it was evidenced the distribution of each element was highlighting homogeneous through of the grain. This experiment was done on several grains with similar results. Similar results were obtained for PFT$_y$-PZT$_{(1-y)}$ by mapping an area of about 700 nm × 400 nm in the lamella (see Figure 6(b)-lower).

G. Magnetoelectric coefficients

Preliminary measurements on bulk ceramic samples of the magnetoelectric coefficients $\alpha_{E,33}$ and $\alpha_{E,31}$ were carried out at 1 kHz and room temperature. The measurements were done for two field orientations: (i) in-plane mode for H and $\delta$H parallel to each other and to the sample plane and perpendicular to $\delta$E and (ii) out-of-plane mode for all the three fields (H, $\delta$H, and $\delta$E) parallel to each other and perpendicular to sample plane. Additional TEM studies done on the same samples in Belfast by Professor J. M. Gregg’s group will be reported in a separate paper. For the 20% PFT/80% PZT specimen $\alpha_{E,31}$ was found (Figure 7) to be 12 mV (cm Oe)$^{-1}$. This is much smaller than the value for FIB single-crystals cut from our ceramic bulk samples; the lower value presumably arises from averaging over domains and grains. The measurements of $\alpha_{E,33}$ (lower curve in Fig. 7) are symmetric with respect to change of sign in applied field +H

![Fig. 6](image-url)

FIG. 6. SEM image (upper figure) for: (a) ~1 μm grain of Pb(Fe$_{0.5}$Nb$_{0.5}$)$_x$(Zr$_{0.53}$Ti$_{0.47}$)$_{1-x}$O$_3$ ($x = 0.2$) and (b) lamella of Pb(Fe$_{0.5}$Ta$_{0.5}$)$_y$(Zr$_{0.53}$Ti$_{0.47}$)$_{1-y}$O$_3$ ($y = 0.4$), ceramic samples. Lower figures in (a) and (b) represent the respective elemental concentration (Fe, Pb, Ti, Zr, Nb, Ta, and O) dot maps for each sample.
or $-H$ and therefore arise from a small biquadratic term $P^2M^2$ and not linear magnetoelectricity, which presumably averages to near zero values in this bulk specimen.

H. Theory

The PFT-PZT and PFN-PZT single-phase materials, we discuss here experimentally are not readily amenable to density functional theory (DFT) calculations for two reasons: First, the four B-site ions Zr, Ti, Fe, and Ta or Nb are not ordered, requiring very large unit cells in the simulations; second, the Fe spins are highly clustered, producing strong magnetoelectricity above the temperature at which long-range magnetic ordering occurs. In this respect these systems are probably good candidates for the Jahn-Teller model of magnetoelectricity,46,47 which is based upon clusters, particularly for perovskite ferroelectrics such as those in the present work.

IV. CONCLUSIONS

In summary, we have successfully fabricate (PbFe$_{0.5}$Nb$_{0.5}$O$_3$)$_x$(PbZr$_{0.53}$Ti$_{0.47}$O$_3$)$_{1-x}$ and (PbFe$_{0.5}$Ta$_{0.5}$O$_3$)$_y$(PbZr$_{0.53}$Ti$_{0.47}$O$_3$)$_{1-y}$ ceramics by solid-state reaction route to produce single-phase room-temperature multiferroic magnetoelectrics. X-ray diffraction analysis and Raman spectra indicate that these PFN-PZT, PFT-PZT systems have perovskite crystal structure. The $T_c$ values decrease from $T_{cPZT} \sim 690$ K toward $T_{cPFN} \sim 385$ K or $T_{cPFT} \sim 240$ K for PFN-PZT or PFT-PZT, respectively, however for all ceramic samples, in this study, the $T_c$ value was above room temperature. Coexistence of biferroic nature i.e., ferroelectric and ferromagnetic properties in PFN-PZT and PFT-PZT systems open the possibility to explore new family of materials which may exhibit the magnetoelectric effect at room temperature. These systems appear superior to bismuth ferrite for device applications in that their dielectric losses are much lower (ca. 1%).

Note added in proof. Evans et al.\textsuperscript{50} measure $5.5 \times 10^{-8}$ sm$^{-1}$ to $1.3 \times 10^{-7}$ sm$^{-1}$ for $\varepsilon_{31}$ in 40:60 PFT/PZT at 293 K. These are very large values. We note also for completeness that PFN-PZT ceramic single-phase compounds were first studied in 1981 by Whatmore and Bell.\textsuperscript{46,49}

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30 S. Kamba, in Nature-sponsored conference on oxides, Aachen, Germany, July 2012.