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Magnetoimpedance and magnetodielectric properties of single phase 45PMN-20PFW-35PT ceramics

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Phase pure and dense polycrystalline 45PMN-20PFW-35PT sample has been synthesized using a columbite precursor method. Structure and surface morphology of the samples were studied using x-ray diffraction and scanning electron microscope. The sample showed the expected reduction in dielectric constant and polarization ($P_{max}=17\ \mu C/cm^2$) compared with that of the parent compound, 65PMN-35PT ($P_{max}=22\ \mu C/cm^2$). The sample is also found to be paramagnetic, which is confirmed by magnetization measurements as a function of temperature and an applied magnetic field. The sample was also tested for magnetoelectric coupling by measuring its dielectric constant and impedance at different applied magnetic fields. The observed colossal negative magnetodielectrics (177%) and colossal positive magnetoimpedance (130%) effect at 7 MHz, which is due to piezoelectric radial vibration. This is an indirect confirmation of the coupling between the electric and magnetic order parameters. © *2010 American Institute of Physics*.

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In the last decade magnetoelectric studies on ferroelectrics that are weakly magnetic[1–4] and magnets that are weakly ferroelectric[5–7] have been done in order to get novel magnetoelectric materials. As far as we know now, there are only a few single-phase materials in nature that possess both ferroelectric and ferromagnetic properties independently.[8] Magnetoelectric multiferroics are at present defined as single phase materials[1–4] or artificially designed nanostructures[9,10] 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.

Lead based ferroelectrics of the form $PbB'_{1/x}B''_xO_3$, for example, the solid solutions of $PbMg_{1/3}Nb_{2/3}O_3$ (PMN) and $PbTiO_3$ (PT) (1-x)PMN-xPT, show relaxor type behavior for $x<0.3$, where the morphotropic phase boundary lies at $x \geqslant 0.35$.[11] PMN-PT ceramics are usually synthesized by sintering a mixture of measured stoichiometric quantities of PbO, MgO, Nb_2O_5, and TiO_2 at high temperatures (1200 °C). However, this conventional solid state route always leads to high amount of Pb loss and formation of pyrochlore phase during high temperature sintering process. Smolenskii *et al.*[12] discovered various multiferroic compounds in the late 1950s, among which lead iron tungstate (PFW) is one of the promising candidates having relaxor behavior below 180 K and antiferromagnetic below 343 K.[13] Recently, multiferroic property has been studied in Pb based compounds such as $PbFe_{0.5}Ti_{0.5}O_3$,[14,15] $Pb(Fe_{0.66}W_{0.33})_{0.5}Ti_{0.5}O_3$,[16] and $Pb(Fe_{0.66}W_{0.33})_{0.8}Ti_{0.2}O_3$.[17,18] In the present work, to avoid Pb loss and formation of pyrocholore phase that normally happens during high temperature sintering, a columbite precursor method was employed to synthesize $0.45(PbMg_{1/3}Nb_{2/3}O_3)-0.20(PbFe_{2/3}W_{1/3}O_3)-0.35(PbTiO_3)$ (45PMN-20PFW-35PT) ceramics at a lower sintering temperature. The ferroelectric, magnetic, dielectric, magnetodielectric, and magnetoimpedance properties of 45PMN-20PFW-35PT ceramics were studied at room temperature.

Polycrystalline 45PMN-20PFW-35PT was prepared by a solid state reaction route through a columbite two-stage calcination method, using native oxides of Pb, Mg, Nb (V), and Ti (IV) of >99% purity as precursors. In the first stage of preparation, MgO, Nb_2O_5, Fe_2O_3, WO_3, and TiO_2 were thoroughly ground into fine powder and first calcined at 1100 °C for 4 h. Addition of MgO in the first stage of synthesis allows it to prereact and mix uniformly with Nb_2O_5 at the atomic level. In the second step, the obtained powders were mixed and ground with stoichiometric amounts of PbO and then the mixture was again calcined at 850 °C for 6 h. This stage was introduced to mix the preheated mixture with PbO to allow thorough diffusion and to facilitate proper mixing of PbO with the columbite mixture. 5 mol % of LiF as sintering aid was subsequently added and mixed along with a few drops of polyvinyl alcohol (PVA) to the final calcined powders. The mixed powder was pressed into pellets (of thickness ~1 mm and diameter 12 mm) under pressure 80 Kg/cm^2 and the pellets were then heated at 600 °C for 3 h to burn out the PVA. Finally the pellets were sintered at various temperatures from 850–925 °C for different time duration 0.5–2 h. The powder x-ray diffraction (XRD) data of the samples were recorded using a PANalytical X'Pert Pro x-ray diffractometer with Cu $K\alpha$ radiation. Morphology and composition analysis of the sample were studied using scanning electron microscope (SEM) and energy dispersive x-ray analysis (EDX). The ferroelectric hysteresis loop (P-E) and magnetization (M-T and M-H) data of the sample were measured using precision premier II ferroelectric loop tracer (Radiant

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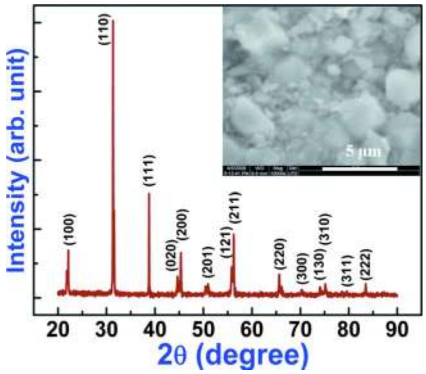

FIG. 1. (Color online) XRD pattern and SEM image (inset) of 45PMN-20PFW-35PT ceramics sintered at 850 °C for 75 min.

Technologies, USA) and physical property measurement system (PPMS, Quantum Design, USA), respectively. Dielectric properties of the sample (12 mm diameter and 1 mm thickness) with an applied magnetic field (0–5 kOe) were measured using impedance analyzer (Agilent 4294A, USA).

Phase pure and dense polycrystalline 45PMN-20PFW-35PT sample was synthesized by a two-stage calcination method, which was also obtained at low sintering temperature (850 °C). In Fig. 1, XRD pattern revealed that the sintered sample at 850 °C for 75 min was single phase and polycrystalline in nature with a tetragonal $P4mm$ symmetry which did not show the presence of pyrochlore impurity phases. The sintering density of the sample was found to be 95% of its theoretical density. SEM image (inset of Fig. 1) of the 45PMN-20PFW-35PT pellet shows the presence of micron sized grains with average size of 3 μm and EDX analysis of the sample showed the obtained compositions are close to that of the nominal compositions.

Figure 2 shows the ferroelectric hysteresis loop (at 4 Hz) of the 45PMN-20PFW-35PT sample obtained at room temperature. The ferroelectric properties of the sample showed an expected reduction in polarization ($P_{max}=17\ \mu C/cm^2$) compared with that of the parent 65PMN-35PT sample ($P_{max}=22\ \mu C/cm^2$). Zero field cooled (ZFC) and field cooled (FC) magnetization measurements of the sample were measured at an applied magnetic field of 1 kOe in the temperature range of 5–350 K (inset of Fig. 3). In the measured temperature range of 5–300 K, FC magnetization values of the sample retrace the ZFC magnetization values, which shows conventional paramagnetic nature which is also confirmed from magnetization versus magnetic field (M-H) measurements at 5 and 300 K (Fig. 3). Dielectric constant (ε_r) and dielectric loss (tan δ) of the sample were measured in the frequency range of 100 Hz–15 MHz [Fig. 4(a)]. A reduction in the dielectric constant compared with that of the parent

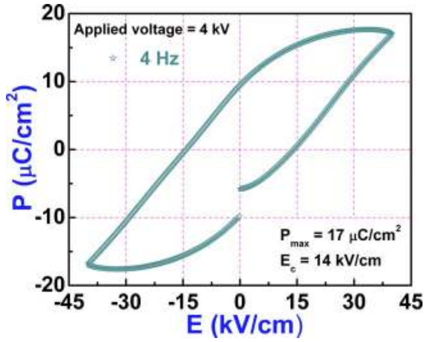

FIG. 2. (Color online) Ferroelectric hysteresis loop (P-E) of 45PMN-20PFW-35PT ceramics at room temperature.

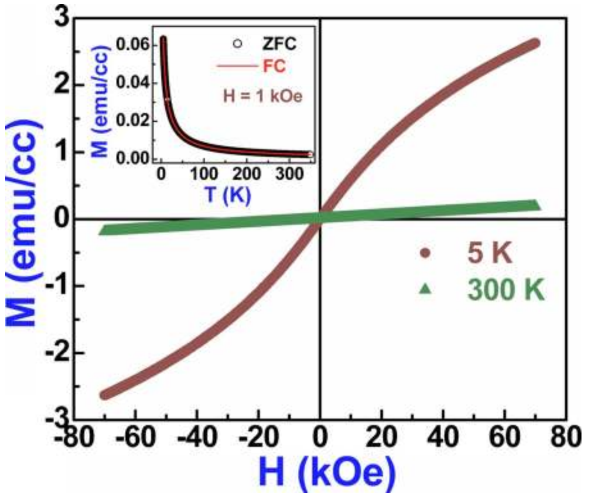

FIG. 3. (Color online) Magnetization vs magnetic field curves of 5PMN-20PFW-35PT ceramics in a magnetic field of 7 T at 5 and 300 K. Inset shows ZFC and FC magnetization measurement of 45PMN-20PFW-35PT ceramics in a magnetic field of 1 kOe.

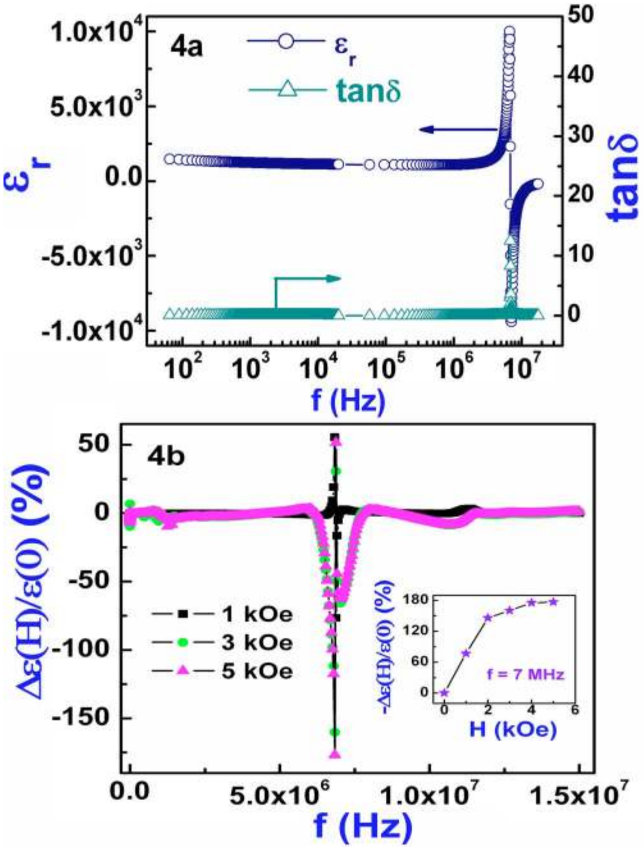

FIG. 4. (Color online) Magnetodielectric properties of 5PMN-20PFW-35PT ceramics in the magnetic field of 1–5 kOe. Left inset shows magnetodielectric effect with an applied magnetic field of the sample at 7 MHz and right inset shows frequency dependant dielectric constant and dielectric loss of the sample.

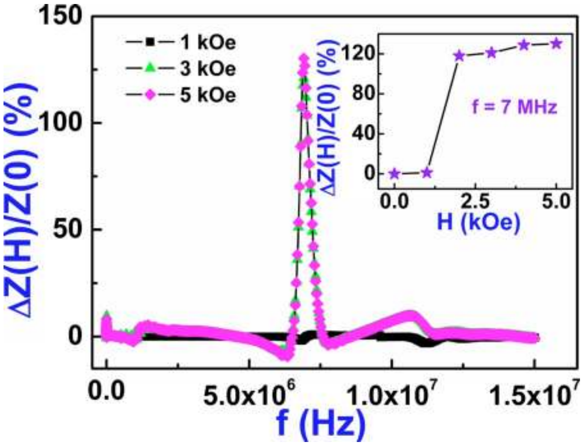

FIG. 5. (Color online) Magnetoimpedance properties of 5PMN-20PFW-35PT ceramics in the magnetic field of 1–5 kOe. Inset shows magnetoimpedance effect with an applied magnetic field of the sample at 7 MHz.

65PMN-35PT was observed and also piezoelectric radial vibration was observed at 7 MHz.

The sample was also tested for magnetoelectric coupling by measuring its capacitance (or dielectric constant) and impedance at different applied magnetic fields (0–5 kOe). The observed colossal negative magnetodielectrics (177%) and colossal positive magnetoimpedance (130%) effect at 7 MHz, which is due to piezoelectric radial vibration [Figs. 4(b) and 5]. The magnetodielectric and magnetoimpedance effects in the sample at 7 MHz were also found to increase with increase in the applied magnetic field and reached a maximum at an applied magnetic field of 5 kOe [inset of Fig. 4(b) and inset of Fig. 5]. The variation in both parameters with an applied magnetic field indirectly confirm the presence of coupling between the magnetic and ferroelectric order parameters in this single phase system of 45PMN-20PFW-35PT.

In conclusion, we synthesized single phase highly dense polycrystalline 45PMN-20PFW-35PT ceramics by columbite two-stage calcination method. Magnetization measurements with temperature (M-T) and magnetic field (M-H) showed that the sample is paramagnetic in nature. Polarization and dielectric constant parameters of the sample were found to reduce compared to that of the parent 65PMN-35PT. The magnetic field dependant dielectric constant and impedance measurements revealed a colossal negative magnetodielectrics (177%) and colossal positive magnetoimpedance (130%) at 7 MHz, which is due to piezoelectric radial vibration. This is an indirect confirmation of the coupling between the electric and magnetic order parameters. This single phase magnetoelectric 45PMN-20PFW-35PT ceramics can find applications in magnetic field sensors and current sensors, etc.

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