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Lead palladium zirconate titanate: A room temperature nanoscale multiferroic thin film

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Abstract

The discovery of single-phase multiferroic materials and the understanding of intriguing physics of the coupling mechanisms between their spin and polarization is important for the next generation of multifunctional devices. In this work, we report dielectric, ferroelectric, and magnetization results of Pd-substituted room-temperature magnetoelectric multiferroic $\text{Pb}(\text{Zr}_{0.20}\text{Ti}_{0.80})_{0.7}\text{Pd}_{0.3}\text{O}_3$ (PZTPd) thin films. Highly c-axis oriented PZTPd thin films were grown on $\{(\text{LaAlO}_3)_{0.3}(\text{Sr}_2\text{AlTaO}_6)_{0.7}\}$ (LSAT) substrates using pulsed laser deposition technique. These films were phase pure and stabilized in tetragonal phase. Atomic force microscopic studies indicated a homogeneous distribution of grains on the films' surface with a surface roughness (R_Q) of ~ 5.4 nm. A large dielectric constant of ~ 1780 and a low loss tangent value of ~ 0.52 were observed at 1 kHz measured at room temperature. Temperature dependent dielectric studies on Pt/PZTPd/ $\text{La}_{0.7}\text{Sr}_{0.3}\text{MnO}_3$ (LSMO) metal-insulator-metal heterostructure capacitors between 80-660 K indicated a diffused ferroelectric to paraelectric phase transition around 515 K. The polarization hysteresis loops observed at room temperature were attributed to its ferroelectric behavior. Saturated magnetization hysteresis loop with remanent magnetization of 1.54 emu/cm^3 was obtained at room temperature. Ferromagnetic ordering in thin films was found to sustain in the entire temperature range from 5-395 K, as revealed from the constant behavior of dM/dT curve with temperature. The mixed oxidation states of palladium ($\text{Pd}^{2+}/\text{Pd}^{4+}$) dispersed in the polar $\text{Pb}(\text{Zr}_{0.20}\text{Ti}_{0.80})\text{O}_3$ matrix were revealed from our high resolution x-rays photoelectron spectroscopic studies, and is ascribed to the origin of ferromagnetic ordering in the film. These findings suggest that PZTPd thin films are multiferroic (ferroelectric-ferromagnetic) at room temperature.

Key words: thin films; multiferroics; magnetization; dielectrics; pulsed laser deposition

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Introduction

Multiferroic materials exhibiting coexistence of at least two ferroic order parameters, such as ferromagnetic, ferroelectricity or ferro-elasticity are the subject of current research interest due to their potential for multifunctional device applications: electronic and memory devices¹⁻⁵. However, only a limited number of single phase multiferroic materials are available due to the chemical incompatibility between magnetic and ferroelectric order parameters and also due to mutual exclusiveness involved in their electronic conditions. A few celebrated examples of multiferroics are: BiFeO_3 ⁶⁻⁸, $\text{Bi}_2\text{FeCrO}_6$ ⁹⁻¹⁰, GaFeO_3 ¹¹, $\text{Pb}(\text{Fe}_{0.5}\text{Nb}_{0.5})\text{O}_3$ ¹², TbMnO_3 ¹³. Most of the single phase multiferroics exhibit multiferroicity only below room temperature. Room temperature multiferroics are important for device applications point of view; however, only a few materials⁶⁻¹¹ are known to exhibit multiferroicity at room-temperature. BiFeO_3 is the most extensively studied room-temperature multiferroic⁶ that exhibits ferroelectric phase transition temperature $T_c \sim 1143$ K and antiferromagnetic Néel temperature $T_N \sim 643$ K, but this material has limited practical applications due to its weak magnetization and magnetoelectric coupling. Therefore, the quest for new single-phase room temperature multiferroic materials have been extensively pursued. $\text{Pb}(\text{Zr}_{0.20}\text{Ti}_{0.80})\text{O}_3$ (PZT) is known to be a robust ABO_3 type perovskite ferroelectric material¹⁴⁻¹⁵. The A-site sublattice is occupied by Pb^{2+} cation, and B-site is occupied by Zr^{4+} and Ti^{4+} cations. Recently, 30% Palladium (Pd) substitution in PZT ceramics was successfully synthesized, that is established to be room-temperature multiferroic¹⁶. Interestingly, Pd atom is non-magnetic, but when it substituted at A-site (Pb^{2+}) and B-site (Zr^{4+} , Ti^{4+}) cations; ferromagnetic ordering was found to organize in the polar PZT matrix. Remarkably, density functional theory (DFT) calculations support ferromagnetism arising from Pd cation substitution in PZT.^{16,17} The results of these calculations revealed that isoelectric cationic substitution, such as Pd^{4+} on B-site cations and/or Pd^{2+} on A-site (Pb^{2+} cation) do not produce magnetism. However, anisoelectric Pd^{4+} substitution at A-site (Pb^{2+} cation) establishes magnetism in the ferroelectric PZT matrix. In other words, the computational results suggest that the mixed oxidation states of Pd cation ($\text{Pd}^{2+}/\text{Pd}^{4+}$) in polar PZT is essential to realize magnetic ordering. Substitution of Pd cation at B-site of the perovskite is common as their radii are almost similar, while Pd^{4+} substitution in A-site (oversized Pb^{2+}) is rather uncommon. However, the Pd^{4+} cationic substitution was realized experimentally by following a long time high energy ball milling (> 8 h)¹⁶ which essentially established a favorable chemistry for the formation and stabilization of the material. Recently, as high as 30% Pd substitution in polar PbTiO_3 ceramic¹⁷ was found to establish a robust room temperature magnetoelectric multiferroicity, better than the well-studied room temperature multiferroic BiFeO_3 . Similarly, a single phase of tetragonal 30% Pd-substituted PZT ceramic was prepared by solid state reaction method and it was found to exhibit room-temperature multiferroic behavior. X-ray photoelectron spectroscopic (XPS) studies on these multiferroic oxides identified mixed oxidation states of Pd cation (i.e. Pd^{4+} , Pd^{2+}), that is in accordance with the DFT prediction to realize magnetism. Temperature dependent

dielectric studies in PZTPd ceramic capacitors identified a ferroelectric to paraelectric phase transition¹⁶ at elevated temperature around 570 K. However, thin film fabrication of this intriguing PZTPd multiferroic material and its investigation on multiferroicity are yet to be carried out. Multiferroic thin films are of research interest for their richness in physics and also due to their several multifunctional device applications including spintronics, high sensitive actuators, sensors, and multistate memory devices¹⁸⁻²². In this paper, we report experimental studies on highly oriented $\text{Pb}(\text{Zr}_{0.20}\text{Ti}_{0.80})_{0.7}\text{Pd}_{0.3}\text{O}_3$ multiferroic thin films grown on $\{(\text{LaAlO}_3)_{0.3}(\text{Sr}_2\text{AlTaO}_6)_{0.7}\}$ (LSAT) substrates using pulsed laser deposition (PLD) technique. Consequently, structural, dielectric, ferroelectric, and magnetic ordering behaviors of these thin films were investigated, and their room temperature multiferroic behavior was established. Ferromagnetism in PZTPd films is ascribed to the mixed oxidation states of Pd cation (i.e. Pd^{2+} and Pd^{4+}) in Pd-substituted polar PZT matrix. Temperature dependent dielectric studies on Pt/PZTPd/LSMO metal-insulator-metal (MIM) heterostructure capacitors indicate a diffused ferroelectric to paraelectric phase transition at around 515 K.

2. Experimental

PZTPd/LSMO and PZTPd thin films were grown on LSAT (001) substrates in an oxygen atmosphere using a KrF excimer laser operated at wavelength $\lambda = 248$ nm using a pulsed repetition rate of 10 Hz employing PLD technique. PZTPd targets with a stoichiometric molecular formula were prepared using solid-state reaction method following the procedure reported earlier.¹⁶ The optimized PLD deposition parameters for the growth of thin films are summarized in **Table 1**.

Table 1 Optimized deposition parameters for $\text{Pb}(\text{Zr}_{0.20}\text{Ti}_{0.80})_{0.7}\text{Pd}_{0.3}\text{O}_3$ thin films using pulsed laser deposition technique.

Substrate	$\{(\text{LaAlO}_3)_{0.3}(\text{Sr}_2\text{AlTaO}_6)_{0.7}\}$ (001)
Target	$\text{Pb}(\text{Zr}_{0.20}\text{Ti}_{0.80})_{0.7}\text{Pd}_{0.3}\text{O}_3$
Target diameter	2.5 cm
Substrate target distance	5 cm
Growth temperature	923 K
Base vacuum	$\sim 10^{-6}$ Torr
O ₂ partial pressure	200 mTorr
Laser source	Excimer (KrF, $\lambda = 248$ nm)
Laser energy used	250 mJ
Pulse repetition rate	10 Hz
Total number of shots	3000
Post deposition <i>ex-situ</i> annealing	923 K for 1 hour in O ₂ atmosphere

Elemental compositions and their mapping distributions in thin film surfaces were studied using Energy Dispersive X-ray Spectroscopy (EDS) using a scanning electron microscope (JEOL JSM-6480LV). The

surface topography of thin films was obtained using Atomic Force Microscopy (AFM-Veeco) operated in a contact mode and their surface roughness was obtained. The phase formation and plane orientation of these grown thin films were inferred from the analysis of high-resolution XRD data obtained using a Smartlab x-ray diffractometer employing a Cu-K α monochromatic radiation ($\lambda = 1.5405 \text{ \AA}$). The chemical oxidation states of the compositional elements were studied using x-ray photo emission spectroscopy (XPS). EDS mapping and diffraction in a short range (nm) were carried out using a Talos TEM/STEM operating at 200 kV. TEM Specimens were prepared using a Tescan FIB microscope. PZTPd capacitors sandwiched between a conducting bottom LSMO layer and a top platinum (Pt) electrode were fabricated to investigate their dielectric and polarization behavior. Top Pt electrodes were fabricated using D.C. sputtering technique and a metal shadow mask of area $100 \mu\text{m} \times 100 \mu\text{m}$ followed by annealing at 650 K in an oxygen atmosphere in order to recover from any defects created during sputtering. Temperature dependent dielectric properties, such as capacitance and dielectric loss tangent ($\tan \delta$) were measured at several frequencies (100 Hz to 1 MHz) in the temperature range of 100-670 K by using an impedance analyzer (HP 4294A) and a MMR K-20 temperature controller (temperature stability of $\pm 1 \text{ K}$). Ferroelectric polarization hysteresis loops were measured at room temperature using a hysteresis loop tester (radiant Technologies RT6000 HVS). Magnetization measurements, such as M-H hysteresis loop, zero-field cooled and field cooled magnetization were carried out using a physical properties measurement system (PPMS, Quantum design) in the VSM module in the temperature range 5-395 K.

3. Results and discussion

Figure 1. (a) x-ray diffraction pattern measured in θ - 2θ geometry for a $\text{Pb}(\text{Zr}_{0.20}\text{Ti}_{0.80})_{0.7}\text{Pd}_{0.3}\text{O}_3$ film grown on LSMO coated LSAT substrate. The reflection peaks are also indexed, and (b) AFM image of $\text{Pb}(\text{Zr}_{0.20}\text{Ti}_{0.80})_{0.7}\text{Pd}_{0.3}\text{O}_3$ films, Inset: 3D-plot of surface morphology.

The phase stability and orientation of these grown thin films were obtained from the analysis of the high-resolution x-ray diffraction pattern measured using Smartlab x-ray diffractometer employing a $\text{Cu-K}\alpha$ radiation ($\lambda = 1.5405 \text{ \AA}$). A typical diffraction pattern is depicted in **Fig. 1a**. As in pristine $\text{PbZr}_{0.20}\text{Ti}_{0.80}\text{O}_3$ ¹⁴, these thin films were found to stabilize in the tetragonal phase ($P4mm$) with their (001) plane parallel to the substrate surface. The prominent reflection peak positions PZTPd (002) was used in Bragg's equation to estimate the out-of-plane lattice parameter c of the films as $4.042(1) \text{ \AA}$. The error in the out-of-plane lattice parameter c was calculated using the standard deviation involved in the 2θ peak position obtained from the fitting of the peak using Voigt function. The lattice mismatch between the PZTPd film and the substrate introduces a structural strain (η) on the thin film, that can be estimated using the relation²³, $\eta = (a_{\text{substrate}} - a_{\text{film}}/a_{\text{film}}) \times 100$. At room temperature LSAT and LSMO are stabilized at cubic perovskite phase with their crystallographic lattice parameters $a_{\text{substrate}} = 3.868 \text{ \AA}$ ²⁴, and $a_{\text{LSMO}} = 3.871 \text{ \AA}$ ²⁴, respectively. In the absence of in-plane x-ray diffraction and/or Reciprocal Space Mapping measurements, the in-plane lattice parameters (a and b) of the films could not be calculated and thereby the in-plane lattice strain in the films can not be estimated. Employing an XP-200 Profilometer, the thickness of the thin films was found to be 300 nm. Surface topography of the films measured over a surface area of $5 \mu\text{m} \times 5 \mu\text{m}$ using an Atomic Force Microscopy (AFM-Veeco) operated in the contact mode, is depicted in **Fig. 1b**. The surface is found to be smooth and crack free with root mean square roughness (R_q) of $\sim 5.4 \text{ nm}$. Energy Dispersive x-ray Spectroscopic (EDS) studies on the films suggested presence of all the constituent elements on the film surface (**Fig. 2a**) and those are found to be around 15% compositional deviation from the target, nearly stoichiometric with the target. Their planar elemental mapping distributions (**Fig. 2b**) over the large surface of the films were found to be uniform. Our recent studies on Transmission Electron Microscopy based high angle annular dark field (HAADF) image and net intensity EDS maps of the constituent elements in a region near the film surface is shown in the supplementary data (**Fig. S1**). It is clear that elemental distribution in the film is not homogeneous in a short length scales (nm). In particular, it seems that Pd is locally concentrated in regions and depleted in others. This distribution appears to be anti-correlated with the Ti map and suggests substitution of Pd cations on the B -site in place of the Ti cations. Given the short length scales over which this heterogeneity occurs, it is likely that an initial solid solution of PZTPd, resolved into a two-phase exsolution upon cooling of the films with elemental variation on the B -site. Moreover, it is suggestive from our selected area electron diffraction studies (**Fig. S2**) that the crystal structure of the films is homogeneous, in spite of the chemical heterogeneity.

Figure 2. (a) EDS spectrum of $\text{Pb}(\text{Zr}_{0.20}\text{Ti}_{0.80})_{0.7}\text{Pd}_{0.3}\text{O}_3$ films shows the presence of all constituent elements at their respective characteristic energy levels. Inset: SEM in-plane image, and (b) Distribution mapping of constituent elements and their sum total elemental mapping from a large planar surface area of thin films.

For dielectric measurements, PZTPd heterostructure capacitors were fabricated by sandwiching the films between the bottom conducting LSMO buffer layers, and the top platinum (Pt) electrodes.

Temperature dependent dielectric behavior, such as capacitance and dielectric loss tangent ($\tan \delta$) were measured at several frequencies (100 Hz to 1 MHz) in the temperature range between 100-660 K (**Fig. 3a**). At room temperature, dielectric constant, and loss tangent values were found to be ~ 1780 , and ~ 0.52 , respectively, measured at the frequency of 1 kHz. The dielectric constant, ϵ , was found to be larger than those reported for ceramics samples PZTPd ($\epsilon \sim 300$)¹⁶, and PbPdT ($\epsilon \sim 500$)¹⁷. One can notice that a moderate decrease in dielectric constant and a nearly constant loss tangent values up to as high as frequency of 10^5 Hz. However, a significant decrease in dielectric constant and a substantial rise in dielectric loss were observed above the frequency 10^5 Hz. The reduction in ϵ is expected due to two contributions: (a) intrinsic contribution which essentially depends on the grain size, orientation, and strain in the film, and (b) extrinsic contributions arise from the grain boundaries, and interface layer. The interface between PZTPd film and LSMO bottom electrode acts as a pinning center²⁴ that perturbs domain wall motion by generating internal electric field; consequently, that reduces extrinsically the dielectric behavior of the capacitors. Earlier dielectric studies on pure LSMO thin films²⁵ suggest that the extrinsic interfacial contribution is significant at high frequencies. **Figure 3a** shows that the dielectric constant increases slowly with rising temperature from 100 to 400 K, and thereafter a rapid increase in ϵ is noticed up to 515 K, which could be resulting from easy orientation of dipoles near the Curie temperature. Low dielectric losses ($\tan \delta < 0.7$) were observed up to 660 K for high frequencies (> 1 kHz). $\tan \delta$ is appeared as a peak with center around 515 K for low frequencies (< 1 kHz), suggesting that the Curie transition temperature (T_c) is around 515 K, as depicted in **Fig. 3b: inset**. The substantial increase in loss tangent $\tan \delta$ value for large frequencies ($> 10^5$ Hz) at high temperatures (> 600 K) can be attributed to oxygen vacancies and several other defects present in the material²⁶. Another possibility of increasing tangential loss could be due to additional capacitance¹⁴ arising from the conducting LSMO bottom layer at high frequencies. Temperature dependent dielectric constant measured at several frequencies are shown in **Fig. 3b**. The dielectric constant is almost insensitive up to 400 K and a broad dielectric peak around 515 K is noticed, which can be attributed to the ferroelectric-paraelectric phase transition temperature T_c (as clearly evident from loss tangent peak, **Fig. 3b:inset**). As mentioned earlier, such ferroelectric-paraelectric phase transition in PZTPd ceramic pellets was reported to be around 570 K¹⁶. Often broadening of dielectric peak over a wide temperature range suggests a diffused phase transition in ferroelectric materials²⁷. The observed broadening of the depicted dielectric peak is expected due to substitutional disorder at the cation sites- *A* and *B* of ferroelectric PZT upon substitution of Pd cation, resulting in a wider distribution of polarization relaxation times involved in several polar domains

²⁶.

Figure 3. For $\text{Pb}(\text{Zr}_{0.20}\text{Ti}_{0.80})_{0.7}\text{Pd}_{0.3}\text{O}_3$ thin films (a) Frequency dependence of dielectric constant (ϵ), Inset: loss tangent $\tan \delta$ versus frequency, and (b) Temperature dependent behavior of dielectric constant (ϵ), Inset: dissipation factor $\tan \delta$ versus temperature.

Ferroelectric hysteresis loops (P - E curves) were measured at ambient temperature at several applied electric fields at a frequency of 10 kHz (Fig. 4). The polarization maximum P_{max} and the remanent

polarization P_r were found to increase with increasing electric field up to 1200 kV/cm and are likely to reach a saturation at larger electric field. Other possibility for non-saturation of P - E loops is that the lossy ferroelectric behavior of thin films originating from oxygen vacancies and other involved ionic conduction processes¹⁷. Several Pd-based perovskites have shown larger conductivity due to Pd cation effects^{17,28,29}. In fact, our studies on the leakage current behavior in these thin film capacitors (I - V curve) support significant conductivity with bias voltage (shown below). At the highest electric field (1200 kV/cm), the maximum polarization, remanent polarization, and coercive field E_c of the ferroelectric loop were found to be 142 μCcm^{-2} , 37 μCcm^{-2} , and 247 kVcm⁻¹, respectively. These values are found to be larger than those reported in Pd-doped bulk samples¹⁶. Often in thin films, defects, such as oxygen vacancies, interface layer establish an internal bias field^{30,31} and this electric field is argued to be responsible for the non-saturation of polarization hysteresis loops.

Figure 4. P - E hysteresis loops of Pt/Pb(Zr_{0.20}Ti_{0.80})_{0.7}Pd_{0.3}O₃/LSMO heterostructure capacitors measured at various applied electric field at a frequency of 10 kHz.

The plot on current-voltage (I - V) characteristic curve of the PZTPd thin films, measured in a voltage step of 0.1 V with an elapsed time of 0.5 sec at each voltage step, is shown in **Fig. 5**. Two distinct regions were observed in the I - V characteristic curve. Initially, current increases linearly with applied electric field up to 0.08 MV/cm, reminiscent of the Ohmic conduction behavior, and above 0.08 MV/cm, the current increases exponentially with field, suggesting the Schottky or Poole-Frankel emission type conduction processes³². Above 0.4 MV/cm, a considerable amount of leakage current (> 0.0007 A) in the films was observed, that can be ascribed to extrinsic conductivity that contributes from oxygen vacancies and interface limited conduction processes¹⁷. Analogous leakage current behavior were shown by other thin film oxide capacitors, such as $(\text{Ba}_{0.955}\text{Ca}_{0.045})(\text{Zr}_{0.17}\text{Ti}_{0.83})\text{O}_3$ ³², and BiFeO_3 ³³, fabricated using PLD method.

Figure 5. Variation of leakage current with applied electric field in $\text{Pb}(\text{Zr}_{0.20}\text{Ti}_{0.80})_{0.7}\text{Pd}_{0.3}\text{O}_3$ films. Fitting of two distinct regions: linear (< 0.08 MV/cm) and non-linear regions (> 0.08 MV/cm) have been marked for the (+) ve field curve and separated by a vertical line.

Magnetization measurements were carried out on PZTPd thin films in in-plane configuration (magnetic field applied parallel to surface of thin films) in the temperature range of 5-395 K. **Figure 6** depicts the magnetization hysteresis curves (M - H curves) for the PZTPd films at different temperatures. The films exhibited discernable and saturated square shaped magnetic hysteresis loops indicating establishment of ferromagnetic ordering in the films. At the lowest temperature of 5 K, the saturation magnetization M_S and the coercive field H_c were found to be 2.61 emu cm^{-3} and 216.31 Oe, respectively. A monotonous decrease of the coercive field H_c and the remanent magnetization M_R were found with increasing temperature (**Fig. 6:inset**), which could be due to thermal energy induced spin disorder³⁴ as expected in ferromagnetic system. At ambient (300 K), the coercive field H_c was found to reduce about 2 times than that observed at 5 K, while the remanent magnetization M_R was found to be nearly 1.6 times less compared to that at 5 K.

Figure 6. M - H hysteresis loops measured at 5 K, 300 K and 395 K. Temperature dependencies of M_R and H_c inseted in lower panel.

Inspection of these hysteresis loops indicates that the magnetization values increase up to an applied field of 900 Oe, and at subsequent high fields ($> 900 \text{ Oe}$), the magnetization growth appears to weaken. The observation of a low coercive and a larger saturation magnetic fields indicate soft magnetic nature of thin films. The larger tails in the M - H loops are due to the dominance of diamagnetic behavior at high magnetic

fields. The observation of magnetic hysteresis loop at 395 K indicates that the thin films are still ferromagnetic at the highest temperature with Curie phase transition temperature above 395 K. It can be mentioned here that the presence of diamagnetic contribution to hysteresis loops is expected for all temperatures. However, this contribution is appreciable for loops at high temperatures only (**Fig. 6**) since the ferromagnetic contribution decreases due to thermal induced spin disorder. The magnetization versus temperature (M - T) curves measured at 100 Oe in zero-field-cooled (ZFC), and field-cooled (FC) conditions revealed a clear bifurcation in these curves with no sharp feature up to 395 K (**Fig. 7a**), reflecting characteristic behavior of the ferromagnetic ordering in the films with absence of any magnetic phase transition. To examine any change in magnetic ordering in the films, we have also investigated the thermal evolution of magnetization in the entire temperature range 5-395 K. For this study, the films were allowed to attain a stable temperature of 5 K (the lowest temperature) in the absence of magnetic field. At the lowest temperature 5 K, a saturation magnetic field of 0.5 T was applied to align the magnetization completely along the applied field direction. Subsequently, the applied magnetic field was turned off and the temperature evolution of magnetization was measured from 5-395 K. In the absence of magnetic field ($H = 0$), thermal evolution of magnetization in the heating cycle is shown in **Fig. 7b**. A gradual reduction of magnetization upon heating is apparent, suggesting the films are ferromagnetic up to 395 K, the highest temperature. The rate of change of magnetization with temperature (dM/dT), insets in **Fig. 7b**, is found to be constant (flatten) with temperature. In general, any changes in the magnetic ordering in films upon rising temperature would have been resulted in a notable change in the dM/dT curve. The fact that the dM/dT magnetization curve remains constant, it is obvious that there is no change in magnetic ordering up to 395 K, and the films are ferromagnetic in the entire temperature range.

Figure 7. (a) Zero-field-cooled and field-cooled M - T curves measured at applied magnetic field H of 100 Oe on $\text{Pb}(\text{Zr}_{0.20}\text{Ti}_{0.80})_{0.7}\text{Pd}_{0.3}\text{O}_3$ films, (b) Temperature evolution of the remanent magnetization generated at 5 K with an applied field of 0.5 T on $\text{Pb}(\text{Zr}_{0.20}\text{Ti}_{0.80})_{0.7}\text{Pd}_{0.3}\text{O}_3$ films. Inset: shows derivative (dM/dT) of magnetization M with respect to temperature T .

As mentioned in the introduction, density functional theoretical studies¹⁶ revealed that the origin of magnetism in PZTPd is due to substitution of Pd^{4+} cations on Pb^{2+} (A-site) of Pb-based perovskite oxides which has been realized experimentally in Pd-substituted oxide multiferroic ceramics recently^{16,17}. A non-isoelectric Pd^{4+} cation replacement for the A-site cation resulted in donation of two free electrons to the defect states in the energy band gap²¹ and these electrons are mainly responsible for the establishment of magnetism in the films. To confirm the chemical states of Pd cations in our thin films, x-ray photo emission spectroscopic studies were carried out. The high resolution XPS spectrum of Pd has two components originated from spin-orbit coupling effect (**Fig. 8**). The spin-orbit doublet of Pd, namely Pd $3d_{5/2}$ and Pd $3d_{3/2}$ are located at the peak center around 337.81 eV and 342.96 eV (**Fig. 8**), respectively. These peaks were found to be asymmetric, suggesting that palladium in thin films are in both Pd^{4+} and Pd^{2+} oxidation states. The Pd $3d_{5/2}$ peak was resolved into Pd^{2+} and Pd^{4+} states with their centers around 337.59 eV and 338.13 eV, respectively. Similarly, the deconvolution of Pd $3d_{3/2}$ peak yielded two components Pd^{2+} and Pd^{4+} states with their respective binding energy of 342.74, and 343.28 eV (**Fig. 8**). The resultant area of the peaks involving Pd^{4+} chemical state was found to be larger than that of the Pd^{2+} state with their ratio being estimated as 1.2:1. Therefore, the observed magnetization in PZTPd thin films (as discussed above) is possible due to occupation of nonisoelectric Pd^{4+} cation on Pb^{2+} (A-site) site, and $\text{Zr}^{4+}/\text{Ti}^{4+}$ (B-site), which is in corroboration with our earlier DFT results¹⁶ revealing ferromagnetism.

Figure 8. x-ray photoelectron spectroscopic analysis for the Pd atom. The individual deconvoluted peaks of Pd 3d_{5/2} and Pd 3d_{3/2} doublet of Pd 3d spectrum are also shown.

4. Conclusions

We synthesized (001) oriented $\text{Pb}(\text{Zr}_{0.20}\text{Ti}_{0.80})_{0.7}\text{Pd}_{0.3}\text{O}_3$ thin films on LSAT, and LSMO buffered LSAT single crystal substrates using pulsed laser deposition technique. These films were phase pure and stabilized into the tetragonal phase. Temperature dependent dielectric spectroscopic studies in a wider temperature window suggest a diffused ferroelectric to paraelectric phase transition around 515 K. The leaky polarization hysteresis loops were attributed to oxygen vacancies and interface limited conduction processes. Saturated magnetization hysteresis loop with remanent magnetization of 1.54 emu/cm^3 was observed at room temperature. The films retain ferromagnetic ordering in the entire temperature range (5 K-395 K). XPS studies suggest that mixed chemical states of palladium cations ($\text{Pd}^{2+}/\text{Pd}^{4+}$) in the polar $\text{Pb}(\text{Zr}_{0.20}\text{Ti}_{0.80})\text{O}_3$ matrix exist and these are responsible for establishing ferromagnetism in PZTPd films. The present experimental studies revealed that the PZTPd thin films are multiferroic at room temperature and these have potential for device applications in non-volatile memories, and actuators.

Supplementary Material

See supplementary material for the complete transmission electron microscopy results of the studied PZTPd thin films.

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Additional Information

Competing Interests: The authors declare no competing interests.

Table captions

Table 1 Optimized deposition parameters for $\text{Pb}(\text{Zr}_{0.20}\text{Ti}_{0.80})_{0.7}\text{Pd}_{0.3}\text{O}_3$ thin films using pulsed laser deposition technique.

Figure captions

Figure 1. (a) x-ray diffraction pattern measured in θ - 2θ geometry for a $\text{Pb}(\text{Zr}_{0.20}\text{Ti}_{0.80})_{0.7}\text{Pd}_{0.3}\text{O}_3$ film grown on LSMO coated LSAT (001) substrates. The reflection peaks are also indexed, and (b) AFM image of $\text{Pb}(\text{Zr}_{0.20}\text{Ti}_{0.80})_{0.7}\text{Pd}_{0.3}\text{O}_3$ films, Inset: 3D-plot of surface morphology.

Figure 2. (a) EDS spectrum of $\text{Pb}(\text{Zr}_{0.20}\text{Ti}_{0.80})_{0.7}\text{Pd}_{0.3}\text{O}_3$ films shows the presence of all constituent elements at their respective characteristic energy levels. Inset: SEM in-plane image, and (b) Distribution mapping of constituent elements and their sum total elemental mapping of large planar surface area of the thin films.

Figure 3. For $\text{Pb}(\text{Zr}_{0.20}\text{Ti}_{0.80})_{0.7}\text{Pd}_{0.3}\text{O}_3$ thin films (a) Frequency dependence of dielectric constant (ϵ), Inset: loss tangent $\tan \delta$ versus frequency, and (b) Temperature dependent behavior of dielectric constant (ϵ), Inset: dissipation factor $\tan \delta$ versus temperature.

Figure 4. P - E hysteresis loops of $\text{Pt}/\text{Pb}(\text{Zr}_{0.20}\text{Ti}_{0.80})_{0.7}\text{Pd}_{0.3}\text{O}_3/\text{LSMO}$ heterostructure capacitors measured at various applied fields with a frequency of 10 kHz.

Figure 5. Variation of leakage current behavior with applied electric field in $\text{Pb}(\text{Zr}_{0.20}\text{Ti}_{0.80})_{0.7}\text{Pd}_{0.3}\text{O}_3$ films.

Figure 6. M - H hysteresis loops measured at 5 K, 300 K and 395 K. Temperature dependencies of M_R and H_c are inseted in the lower panel.

Figure 7. (a) Zero-field-cooled and field-cooled M - T curves measured at applied magnetic field H of 100 Oe on $\text{Pb}(\text{Zr}_{0.20}\text{Ti}_{0.80})_{0.7}\text{Pd}_{0.3}\text{O}_3$ films, (b) Temperature evolution of the remanent magnetization generated at 5 K with applied field of 0.5 T on $\text{Pb}(\text{Zr}_{0.20}\text{Ti}_{0.80})_{0.7}\text{Pd}_{0.3}\text{O}_3$ films. Inset: shows derivative (dM/dT) of magnetization M with respect to temperature T .

Figure 8. x-ray photoelectron spectroscopic analysis for the Pd element. The individual deconvoluted peaks of doublet Pd $3d_{5/2}$ and Pd $3d_{3/2}$ of Pd 3d spectrum are also shown.

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Intensity (arb. units)

Polarization ($\mu\text{C}/\text{cm}^2$)

Intensity (arb. units)