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Design and Development of Novel Room Temperature Multiferroics for Multifunctional Devices

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14. ABSTRACT
We have synthesized and examined the room temperature multiferroicity in lead palladium titanate and established a radical new direction in the multiferroic field. Our findings are in contrast to the popular view that palladium may substitute B-site and not A-site in perovskite oxides and thus not be magnetic. PbTiO3 samples doped with 10% and 30% of Pd were prepared using solid-state reaction method. The phase purity of the samples was confirmed using Rietveld analysis of the recorded x-ray diffraction data.
Compositional analysis of the prepared samples was ascertained from the scanning electron micrograph and energy-dispersive x-ray analysis results. Temperature dependent dielectric spectroscopic data indicate only one peak corresponding to the ferroelectric–to-paraelectric phase transition. Upon Palladium doping, the observed ferroelectric transition temperature Tc is found to be lower, which can be argued due to the changes in the unit cell due to off-centre displacements of the B-site cation. Magnetization measurements as a function of applied magnetic field suggest that Pd-doped samples are ferromagnetic at room temperature. 30% Pd, the highest dopant sample, exhibits larger magnetic moment 2.8×10-4 emug-1. However, the coercivity of 10%Pd, a lesser dopant sample, is observed to be larger. The magnetic Curie temperature is found to be lower than the ferroelectric Curie temperature, viz.; for 30% Pd, the magnetic and ferroelectric Curie temperatures are 450 K and 730 K, respectively. The present work establishes the experimental evidence of room temperature multiferroic in lead palladium titanate materials and suggests its potential applications in non-volatile memories, transducers, and actuators-based devices. To understand the phase stability, we have also studied the high-pressure synchrotron and Raman spectroscopy on multiferroic Pb0.9Pd0.1TiO3 using a diamond anvil cell. It shows a single chemical perovskite phase with two or possibly three subtle structural transitions under pressure up to 15 GPa: the lowest is a tricritical line at P=0.8–2.0GPa; the second is a non-cubic but metrically cubic phase at 1.8GPa; and the highest phase transition is to a true cubic perovskite at ~ 10 GPa.

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We have synthesized and examined the room temperature multiferroicity in lead palladium titanate and established a radical new direction in the multiferroic field. Our findings are in contrast to the popular view that palladium may substitute B-site and not A-site in perovskite oxides and thus not be magnetic. $PbTiO_3$ samples doped with 10% and 30% of Pd were prepared using solid-state reaction method. The phase purity of the samples was confirmed using Rietveld analysis of the recorded x-ray diffraction data. Compositional analysis of the prepared samples was ascertained from the scanning electron micrograph and energy-dispersive x-ray analysis results. Temperature dependent dielectric spectroscopic data indicate only one peak corresponding to the ferroelectric–to-paraelectric phase transition. Upon Palladium doping, the observed ferroelectric transition temperature Tc is found to be lower, which can be argued due to the changes in the unit cell due to off-centre displacements of the *B*-site cation. Magnetization measurements as a function of applied magnetic field suggest that Pd-doped samples are ferromagnetic at room temperature. 30% Pd, the highest dopant sample, exhibits larger magnetic moment 2.8×10-4 $emug^{-1}$. However, the coercivity of 10%Pd, a lesser dopant sample, is observed to be larger. The magnetic Curie temperature is found to be lower than the ferroelectric Curie temperature, viz.; for 30% Pd, the magnetic and ferroelectric Curie temperatures are 450 K and 730 K, respectively. The present work establishes the experimental evidence of room temperature multiferroic in lead palladium titanate materials and suggests its potential applications in non-volatile memories, transducers, and actuators-based devices. To understand the phase stability, we have also studied the high-pressure synchrotron and Raman spectroscopy on multiferroic $Pb_{0.9}Pd_{0.1}TiO_3$ using a diamond anvil cell. It shows a single chemical perovskite phase with two or possibly three subtle structural transitions under pressure up to 15 GPa: the lowest is a tricritical line at P=0.8–2.0GPa; the second is a non-cubic but metrically cubic phase at 1.8GPa; and the highest phase transition is to a true cubic perovskite at ~ 10 GPa.

We have also synthesized thin films of $PbPd_{0.3}Ti_{0.7}O_3$ using Pulsed laser deposition method, and studied their dielectric, ferroelectric, piezo-response force microscopy, and magnetization behavior. Highly oriented $PbPd_{0.3}Ti_{0.7}O_3$ thin films were deposited on $\{(LaAlO_3)_{0.3}(Sr_2AlTaO_6)_{0.7}\}$ (LSAT) substrates in oxygen atmosphere using pulsed laser deposition technique. X-ray diffraction studies revealed that the films had tetragonal phase with c-axis orientation. Surface morphology studies using atomic force and scanning electron microscopy suggest a smooth and homogeneous distribution of grains on the film surface with roughness ~2 nm. Temperature dependent dielectric measurements carried out on $Pt/PbPd_{0.3}Ti_{0.7}O_3$ $/La_{0.7}Sr_{0.3}MnO_3$(LSMO) metal-dielectric-metal capacitors suggest a ferroelectric to paraelectric transition around 670 K. The measured polarization hysteresis loops at room temperature were attributed to its ferroelectric behavior. From a Tauc plot of $(\alpha h\nu)^2$ versus energy, the direct band gap E_g of $PbPd_{0.3}Ti_{0.7}O_3$ thin films was calculated as 3 eV. Ferroelectric piezoelectric nature of the films was confirmed from a strong domain switching response revealed from piezo-response force microscopy. A well-saturated magnetization M-H loop with remanent magnetization of 3.5 emu/cm^3 was observed at room temperature, and it retains ferromagnetic ordering in the temperature range 5-395 K. Origin of the magnetization could be traced to the mixed oxidation states of Pd^{2+}/Pd^{4+} dispersed in polar $PbTiO_3$ matrix, as revealed by our x-ray photoelectron spectroscopic results. These results established that $PbPd_{0.3}Ti_{0.7}O_3$ thin films are multiferroic at room temperature.

c-axis oriented $Pb(Zr_{0.20}Ti_{0.80})_{0.7}Pd_{0.3}O_3$ thin films on $\{(LaAlO_3)_{0.3}(Sr_2AlTaO_6)_{0.7}\}$ substrates were also synthesized utilizing PLD technique. These films were found to be phase pure and stabilized in a 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. Temperature dependent dielectric studies on metal–insulator–metal heterostructure capacitors 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 to 395 K, as obtained from the constant value of the dM/dT curve with temperature. Coexistence of oxidation states of palladium (Pd^{2+}/Pd^{4+}) dispersed in the polar $Pb(Zr_{0.20}Ti_{0.80})O_3$ matrix were revealed from our high resolution x-ray photoelectron spectroscopic studies and is ascribed to the origin of ferromagnetic ordering in the film. These findings indicates that $Pb(Zr_{0.20}Ti_{0.80})_{0.7}Pd_{0.3}O_3$ thin films are multiferroic at room temperature.

Since phase dependence of material properties and unraveling the physics behind the transition is useful for desirably tuning the physical properties, we have also established a phase diagram of technologically important multiferroic $(1-x)Pb(Fe_{0.5}Nb_{0.5})O_3-xNi_{0.65}Zn_{0.35}Fe_2O_4$ (x = 0,0.1,0.2 and 0.3) using our bulk and local measurement of ferroelectric data. This composite material consists of a perovskite and a spinel compound. It exhibits strong ferroelectric and magnetic properties with large magnetoelectric coupling above room temperature. Polycrystalline thin films (x = 0-0.3) were grown on $LaNiO_3$ buffered $(LaAlO_3)_{0.3}(Sr_2AlTaO_6)_{0.7}$ substrate. Temperature dependent dielectric permittivity measurement probed the ferroelectric transition temperatures in the range 400-460 K. Upon increasing x, enhancement in the transition temperature is attributed to compressive epitaxial strain on thin films. Local measurement of ferroelectric loop using piezo response force microscopy yield hysteresis loops as a function of temperature below the Curie temperature. These experimentally realized phases (ferroelectric-to-paraelectric) are realized using the theoretically predicted results using Gaussian process regression model.

Another system of interest is $BiFeO_3$ (BFO) based multiferroics, which is a widely studied room temperature multiferroic. However, it possesses high leakage current and large coercive field due to the presence of charge defects and oxygen vacancies which essentially causes its poor ferroelectric properties. In our studies, we established an improvement of ferroelectric and photovoltaic properties of (Nd, V) cationic co-doped $BiFeO_3$ thin films. The optical band gap of BFO is 2.67 eV, lower than that observed in other perovskite materials such as $BaTiO_3$, $LiNbO_3$ etc; suggesting its suitability for advanced optoelectronic and photovoltaic applications. In order to improve its ferroelectric and photovoltaic properties, we have synthesized the Nd^{3+} and V^{5+} co-doped $Bi0.95Nd_{0.05}(Fe_{1-x}V_x)O_3$ (x =0.01, 0.03) thin films on $Pt/TiO_2/SiO_2/Si$ substrates using pulsed laser deposition technique. Analysis of x-ray diffraction results suggests phase purity of the sample. Elemental analysis suggests compositional uniformity of the thin films. XPS results for x = 0.03 indicates that Fe ion has only 3+ valency, contrary to x = 0.0, 0.01 compounds, and thereby extinguishing oxygen vacancies in this highest concentration sample was concluded. Piezo response force microscopy-based studies on ferroelectric properties in the nanoscale suggest a complete polarization switching for x = 0.3 as compare to pristine sample, which is understood in the line of dominance of polarization flipping over oxygen vacancies. The investigation on the photovoltaic effect on thin films indicates that an enhancement in photovoltaic response for x = 0.03

compound than pristine one. In addition, the photo current J_{SC} and photo voltage V_{OC} are observed to be stable with time for $x = 0.03$ composition. Improved in photovoltaic response with dopant is found to be associated with the less recombination of hopping electrons and oxygen vacancies. The role of oxygen vacancies on the photo responsive behaviours is evident from this investigation.

We have also investigated the doping effect on magnetic behaviour on $SmCrO_3$, which is still at large. Pristine rare-earth orthochromate is known to be multiferroics. Anti-ferromagnetic spins order of Cr^{3+} magnetic ion occurred ~192K. Evidence of colossal dielectric behaviour in the order of ~10^4 is reported. The co-doping of magnetic ions Gd^{3+} and Mn^{3+} on the magnetic behaviour of multiferroics $SmCrO_3$ were investigated. Gd = 0.1 and Mn = 0.15 substituted $Sm_{0.9}Gd_{0.1}Cr_{0.15}Mn_{0.85}O_3$ polycrystalline samples were prepared by solid state reaction method. Rietveld refinement analysis on x-ray diffraction pattern suggests single phase of the compound, stabilizes at orthorhombic perovskite (Space group *Pnma*) phase. Temperature dependent magnetization (M~H) curves were measured in zero field cooled and field cooled (FC) conditions at applied field H = 50, 1000, 2500, and 5000 Oe. In FC condition, for the applied field up to H = 2500 Oe, the magnetization crosses zero value at T ~105 K and become positive below spin orientation temperature T_{sr} ~17 K. Upon further enhancement in applied field to H = 5000 Oe, magnetization becomes positive in the entire temperature range 2-300 K. This is understood in the line of rotation of the magnetic moments of Mn^{3+} and Sm^{3+}/Gd^{3+} ions along the applied field direction. Temperature dependent M~H hysteresis curves were measured in the field up to H = ±90 kOe in the temperature range 2-80 K. The hysteresis loops were found to be symmetrically closed and were not saturated. Due to the coexistence of high field antiferromagnetic and low field weak ferromagnetic, the maximum loop opening was seen around the spin re-orientation temperature T_{sr}. Estimation of magnetocaloric effects, which essentially manifested in its change in magnetic anisotropy (ΔS), were carried out using the 1st quadrant *M-H* curves data. At low temperature, the change in entropy ΔS is found to be 16 times (sixteen times) higher than the pristine $SmCrO_3$ compound; hence, a significant enhancement in magnetocaloric properties was evident.

Interesting search on near room temperature green multiferroic is the current trend of research. In this aspects, mmultiferroic Gallium Ferrite ($GaFeO_3$, GFO), known to be piezoelectric, and ferrimagnetic near room temperature with significant magnetoelectric (ME) coupling (10^{-11} s/m at 4.2 K) is a candid material. In view of this, we have studied the coupled magnetic ordering and phonons in Gallium Ferrite using magnetization and inelastic light scattering measurements as a function of temperature (82-570 K). Single phase GFO polycrystalline samples stabilizes in orthorhombic phase (space group C_{2v}^9) were prepared by solid-state reaction method. Temperature-dependent magnetization studies in the temperature range of 5-395 K at field-cooled (FC) and zero-field-cooled (ZFC) conditions using different static magnetic fields confirms the magnetic transition temperature Tc at 220 K. Evidence of spin-glass-like magnetic ordering is apparent at low temperature. Temperature-dependent Raman spectrum at 82 K showed 31 Raman active modes in the spectral range 90–900 cm^{-1}. Some of the phonon mode frequencies exhibit anomalies close to T_C. At elevated temperatures, no significant changes in Raman spectra were observed that can be attributed to the absence of structural phase transition. Instead of expected anharmonic behavior, several librational and stretching modes of rigid BO_6 units were found to be hardening below Tc, suggesting the significant magnetoelastic coupling contributions to phonon frequencies. Magnetic excitation induced phonon renormalization is evident in the low temperature magnetic phase. Many phonon modes located at 153, 176, 240, 700, and 756 cm^{-1} are found to have magnetoelastic coupling contributions below the T_C. The spin-phonon coupling strength is found to be larger for internal mode located at 700 and 756 cm^{-1} i.e. λ ~ 2.14 and 2.92, respectively. Translational modes at 153 and 175 cm^{-1} and the librational rigid mode at

240 cm^{-1} are found to have nearly same coupling strength with $\lambda \sim 0.88$. As known, in thin films, one dimension is reduced (quasi-two-dimensional materials) in nano-scale, results in a possible different ferroelectric and magnetic ordering. Therefore, it is of interest to grow doped GFO thin films and examine its multiferroicity. Highly oriented GFO thin films on $SrTiO_3$ (111) substrate have been fabricated recently to examine their multiferroic properties. GFO thin film shows excellent magnetic and improved ferroelectric behavior near room temperature ~300 K. However, the leakage current effect due to fluctuation of Fe^{2+} and Fe^{3+} cations resulting in leaky ferroelectric behavior. To improve its ferroelectric properties, suitable cation dopants, such as Sc^{3+}, La^{4+} are under investigation.

Perovskite ferroelectric oxides (ABO_3) are known to possess multifunctional properties. Investigations on electrophysical properties of technologically important ferroelectric $Pb(Zr_{0.53}Ti_{0.47})O_3$ (PZT) materials is useful from technological application point of view. Electrophysical properties such as permittivity, ferroelectricity, electrical resistivity, Curie temperature and crystal structure of PZT can be improved by substitution of isovalent and/or heterovalent ion either at A and/or B-site. In this regard, we have studied the PZT based systems both in ceramics and thin films. Intentionally A-site of PZT was doped with 10% Sc^{3+} and 5% Pb were made vacant. The idea was to dilute the oxygen vacancies concentration (Vö) and compensate Pb vacancies (Vpb) mediated hole by the donors. Solid state synthesis of a single-phase compound was found to be stabilizes at tetragonal crystal (*P4mm*) with a reduced tetragonality c/a = 1.005. Raman spectroscopic studies identify the soft optical phonons responsible for ferroelectric to paraelectric phase transition around ~460 K. Robust dielectric and ferroelectric behaviour were elucidated form our studies. Subsequently, we have also investigated Sc^{3+} and La-substituted $Pb(Zr_{0.53}Ti_{0.47})$ oriented nanoscale films for energy storage applications. Highly oriented $0.90[PbZr_{0.53}Ti_{0.47}]$ $0.10[La_{0.80}Sc_{0.20}]O_{3-\delta}$ (PLZTS), and La^{3+} & Sc^{3+} mixed doped $Pb(Zr_{0.53}Ti_{0.47})_{0.90}Sc_{0.10}O_{3-\delta}$ (PZTS) thin films were deposited on LSMO buffer layer coated MgO (100) substrate by following two subsequent laser ablation processes in oxygen atmosphere employing pulse laser deposition. These films were found to grow in tetragonal phase with orientation along (100) plane as inferred from x-ray diffractometry analysis. The structural sensitive symmetric E (LO_2) Raman band softened at elevated temperature along with its intensity continuously decreased until it disappeared in the cubic phase above 350 K. The existence of broad Raman bands at high temperature (> 350 K) is attributed to the symmetry forbidden Raman scattering in relaxor cubic phase due to symmetry breaking in nano length scale. The temperature dependent dielectric measurements were performed on fabricated LSMO/PZTS/Pt metal-ferroelectric-metal capacitors in the frequencies range 10^2-10^6 Hz was observed to be diffused over a wide temperature range of 300-650 K and exhibited a high dielectric constant of ~5700 at room temperature. We observed slim polarization hysteresis loops at several frequencies attributed to relaxor behavior of PZTS and PLZTS thin films. Using the hysteresis loop on PZTS, an excellent high energy storage density (U_{re}) ~ 52 J/cm^3 with efficiency η ~70 % was estimated. On the other hand, ~19 J/cm^3 with efficiency η ~66 % was found for mixed doped La^{3+} and Sc^{3+} based PZT. High DC breakdown strength, larger dielectric constant and larger restored energy density values of these thin films indicate its possible use as an efficient thin films' material for high energy storage applications.

Another system of our interest was $SnTiO_3$, which is a room temperature ferroelectric with large polarization. This material is an environmentally friendly ferroelectric perovskite since it does not contain toxic Pb cation. However, preparation of single phase $SnTiO_3$ thin film is difficult due to availability of both Sn^{2+} and Sn^{4+} cations originated during synthesis processes using conventional PLD and other high temperature techniques. In our studies a single phase $SnTiO_3$ thin films were prepared by using our state-of-art atomic-layer deposition method using a P-type (001) Si-substrate and their ferroelectricity and photovoltaic effects were investigated. A well-defined polarization hysteresis loops at room temperature was observed. Temperature dependent dielectric studies suggest a transition from a ferroelectric relaxor to a paraelectric phase around 500 K. The optical band gap is estimated as 2.6 eV from UV-Vis spectroscopic results. Interestingly, a photo-induced enhancement in spontaneous polarization was noticed and indicates the photoelectric nature of the titular films. Our studies on ALD-based thin films on $SnTiO_3$ establish a path to develop green ferroelectrics for nano electric devices and photo-ferroelectric applications.

Notably, the intriguing coupling phenomena among spin, phonon, and charge degrees of freedom in materials having magnetic, ferroelectric and/or ferroelastic order have been of research interest for the fundamental understanding and technological relevance of magnetoelectric materials. We have carried out a detailed study on structure and phonons of $Al_{0.5}Ga_{0.5}FeO_3$, a lead-free magnetoelectric material, employing variable temperature dependent powder neutron diffraction and Raman spectroscopy. Neutron diffraction studies suggest that Al^{3+} ions are distributed in one tetrahedrally (BO_4) and three octahedrally (BO_6) coordinated sites of the orthorhombic (*Pc21n*) structure and there is no structural transition in the temperature range of 7–800 K. Temperature dependent field-cooled and zero-field-cooled magnetization studies indicate ferrimagnetic ordering below 225 K (T_N), and that is reflected in the low temperature powder neutron diffraction data. An antiferromagnetic type arrangement of Fe^{3+} ions with net magnetic moment of 0.13 μB/Fe^{3+} was observed from powder neutron diffraction analysis and it corroborates the findings from magnetization studies. The deviation of several mode frequencies from the standard anharmonicity model in the ferrimagnetic phase (below 240 K) is attributed to coupling effect between spin and phonon. Spin–phonon coupling effect is discernable from Raman bands located at 270, 425, 582, 695, 738, and 841 cm^{-1}. Their coupling strengths have been estimated using our phonon spectra and magnetization results. BO_n (n = 4, 6) libration (restricted rotation) mode at 270 cm^{-1} has the largest coupling constant, while the stretching vibrations located at 695 and 738 cm1 have the lowest coupling constant. In addition to the libration mode, several internal stretching and bending modes of polyhedral units are strongly affected by spin ordering.

<u>Scientific Articles</u> *(In Referred Scientific Journals)*

<u>2020</u>

2020-1 Lead palladium titanate: A room temperature nanoscale multiferroic thin film, KK Mishra, AA Instan, S Kumari, JF Scott, RS Katiyar, Scientific Reports 10 (1), (2020)1-11.

2020-2 Phonon and magnetoelastic coupling in $Al_{0.5}Ga_{0.5}FeO_3$: Raman, magnetization and neutron diffraction studies, KK Mishra, RR Shukla, PSR Krishna, PD Babu, SN Achary, RS Katiyar, JF. Scott Physical Chemistry Chemical Physics 22, (2020) 6906.

2020-3 Lead palladium zirconate titanate: A room temperature nanoscale multiferroic thin film, K. K. Mishra, Jose A. Hernandez, Alvaro A. Instan, Shane J. McCartan, J. Marty Gregg, and Ram S. Katiyar, J. Appl. Phys. 127, (2020).

2020-4 Progress in designing Novel single phase Room Temperature Multiferroics, Ram S. Katiyar, K. K. Mishra, Review Article, Ferroelectrics (2020).

2019

2019-1 Studies of Multiferroic Palladium Perovskites, Dhiren K. Pradhan, Ajay K. Mishra, Shalini Kumari, Abhisek Basu, Maddury Somayazulu, Elzbieta Gradauskaite, Rebecca M. Smith, Jonathan Gardner, P. W. Turner, Alpha T. N'Diaye, M. B. Holcomb, Ram S. Katiyar, Peng Zhou, Gopalan Srinivasan, J. M. Gregg & J. F. Scott, Scientific Reports volume 9, Article number: 1685 (2019) 2019-2.

2019-2 Coupled phonons and magnetic orderings in GaFeO3: Raman and magnetization studies, Sita Dugu, Karuna Kara Mishra, Dhiren K. Pradhan, Shalini Kumari, and Ram S. Katiyar, Journal of Applied Physics 125, 064101 (2019).

2019-3 Ferroelectric ordering and energy storage density of thin films capacitor by doping La^{3+} and Sc^{3+} on $Pb(Zr_{0.53}Ti_{0.47})O_3$ using pulse laser deposition technique, Mohan K. Bhattarai, Karuna K. Mishra, Sita Dugu, Alvaro Instan, & R. S. Katiyar, Appl. Phys. Lett.114, 0000 (2019) DOI: 10.1063/1.5089224.

2018

2018-1 Reconstructing phase diagrams from local measurements via Gaussian processes: mapping the temperature-composition space to confidence, Dhiren K Pradhan, Shalini Kumari, Evgheni Strelcov, Dillip K Pradhan, Ram S Katiyar, Sergei V Kalinin, Nouamane Laanait, Rama K Vasudevan, NPJ Computational Materials 4, 1 (2018).

2018-2 Observation of magnetization reversal behavior in $Sm_{0.9}Gd_{0.1}Cr_{0.85}Mn_{0.15}O_3$ orthochromites, Neeraj Panwar, Jostin P Joby, Surendra Kumar, Indrani Coondoo, M Vasundhara, Nitu Kumar, Ratnakar Palai, Rahul Singhal, Ram S Katiyar, AIP Advances 8, 055818 (2018).

2018-3 Room-temperature relaxor ferroelectricity and photovoltaic effects in SnTiOx/Si thin film heterostructures, Radhe Agarwal, Yogesh Sharma, Siliang Chang, Krishna Pitike, Changhee Sohn, Serge M Nakhmanson, Christos G Takoudis, Ho Nyung Lee, James F Scott, Ram S Katiyar, Seungbum Hong, Physical Review B 97, 054109 (2018).

2018-4 Modulation of Oxygen Vacancies Assisted Ferroelectric and Photovoltaic Properties of (Nd, V) co-doped $BiFeO_3$ Thin Films Radhe Agarwal, Yogesh Sharma, Seungbum Hong and Ram S. Katiyar, J. Phys. D: Appl. Phys. **51**, 275303 (2018).

2018-5 Effect of Substrate Temperature on Structural and Magnetic Properties of c-axis Ori-ented Spinel Ferrite $Ni_{0.65}Zn_{0.35}Fe_2O_4$ (NZFO) Thin Films, DK Pradhan, S Kumari, DK Pradhan, A Kumar, RS Katiyar, RE Cohen, J. Alloys and Compounds **766**, 1074 (2018).

2017

2017-1 Effect of off-center ion substitution in morphotropic lead zirconatetitanate composition, M K Bhattarai, S P Pavunny, A A Instan, J F Scott, R S Katiyar, Journal of Applied Physics 121 (19), 194102 (2017).

2017-2 PbTi1-xPdxO3: A New Room-temperature Magnetoelectric Multiferroic Device Material, Elzbieta Gradauskaite, Jonathan Gardner, Rebecca M Smith, Finlay D Morrison, Stephen L Lee, Ram S Katiyar, James F Scott, Physical Review B 96, 104104 (2017).

Presentations

2020

1. Designing Novel Room Temperature Single Phase Multiferroics for Multifunctional Applications, International Symposium on "Synthesis and Characterization of Smart Materials and Their Potential Applications" (ISSCSMA-2020): 14-17 June 2020, held at New Delhi, Keynote Speaker.

2019

1. Room Temperature Lead Palladium Titanate Nanoscale Multiferroic Thin Films, K. K. Mishra, Mohan K. Bhattarai, A. A. Instan, R.S. Katiyar, **2019** MRS Fall Meeting and Exhibit (Boston, USA 2019)
2. Nanoscale $\mathbf{V_2O_3}$ films prepared by magnetron DC sputtering: Metal-Insulator phase transition and magnetic ordering, Ivan W. Castillo, Karuna K. Mishra, Ram S. Katiyar **2019** MRS Fall Meeting and Exhibit (Boston, USA 2019)
3. Ferroelectricity and Temperature Dependent Dielectric Response in Rare Earth Doped Lead Zirconate Titanate Nano crystalline Films, Mohan K. Bhattarai, A. A. Instan, K. K. Mishra, R.S. Katiyar, **2019** MRS Fall Meeting and Exhibit (Boston, USA 2019)
4. Room Temperature Lead Zirconium Palladium Titanate Multiferroic Nanoscale Films, K. K. Mishra, Mohan K. Bhattarai, A. A. Instan, R.S. Katiyar, **2019** MRS Fall Meeting and Exhibit (Boston, USA 2019), Invited talk

2018

5. Near Room Temperature Multiferroism in Gallium Ferrite. Sita Dugu, D.K.Pradhan, K.K.Mishra, Shalini Kumari, R.S. Katiyar International conference, **2018** MRS Spring Meeting and Exhibit (Phoenix, USA 2018)
6. High Pressure Behavior of Multilayered Vanadium Diselenide: Grüneisen Parameter, Phase Instability and Thermal Properties. K.K.Mishra, T.R.Ravindran, K.K.Pandey, and R.S.Katiyar **2018** MRS Spring Meeting and Exhibit (Phoenix, USA 2018)
7. Dielectric and Ferroelectric behaviors of PZT Thin Films modified by rare-earth metals (La^{3+}, Sc^{3+}) for Ferroelectric Memory Applications. Mohan K. Bhattari, K. K. Mishra, A. A. Instan, R.S.Katiyar **2018** MRS Spring Meeting and Exhibit (Phoenix, USA 2018)
8. Relaxor-Ferroelectric Behaviors on Rare Earth Modified Lead Zirconate Titanate, Mohan K. Bhattari, A. A. Instan, K. K. Mishra, R.S.Katiyar **2018** MRS Spring Meeting and Exhibit (Phoenix, USA 2018)
9. Phonon and Magneto-electric ordering in Gallium Ferrite multiferroic. Sita Dugu, K. K Mishra, Dhiren K. Pradhan, Shalini Kumari, Ram S. Katiyar **2018** APS March Meeting (Los Angeles, USA 2018)
10. Studies on Magnetic and Electrical Properties of Gallium Ferrite Multiferroic Thin Film, Sita Dugu, Dhiren Pradhan, Shalini Kumari, Mohan Bhattarai, Alvaro Instan, Ram Katiyar **2018** MRS Fall Meeting and Exhibit (Boston, USA 2018)
11. Dielectric and Ferroelectric Behaviors of Modified PZT Thin Films Synthesized by Pulse Laser Deposition, Mohan Bhattarai, Alvaro Instan, Sita Dugu, Pawan Kumar, and Ram Katiyar 2018 MRS Fall Meeting and Exhibit (Boston, USA 2018)

12. Nobel Lead Free Relaxor Multiferroic for High Energy Storage Application, Mohan Bhattarai1 Sita Dugu, Alvaro Instan, and Ram Katiyar 2018 MRS Fall Meeting and Exhibit (Boston, USA 2018)
13. Dielectric and Phonon Behaviors in Lead-Free Advance Ferroelectric [KNbO3]1-x[(BaNi1/2Nb1/2O3-δ)]x Compound, Blanca Rosas, Alvaro Instan, Karuna Mishra, Ram Katiyar, 2018 MRS Fall Meeting and Exhibit (Boston, USA 2018)

2017

1. Ferroelectric/MultiferroicTunnel Junction for Nanoelectronic Devices, RS Katiyar, Invited talk at ISIF New Delhi, Dec 10-13 (2017).
2. Effect of defects, dopant & aging on Electromechanical Coupling in doped $BaTiO_3$, Dhiren K Pradhan, RS Katiyar, ISIF New Delhi, Dec 10-13 (2017).
3. Artificial Multilayers & Superlattices LSMO/PZTFT Heterostructures for Memory Devices Applications Shalini Kumari, RS Katiyar, ISIF New Delhi, Dec 10-13 (2017).
4. Tip-Enhanced Photovoltaic Effects in Pd Substituted PZT Thin Films. Shalini Kumari, Dhiren Pradhan, Ashok Kumar, Ram Katiyar, MRS Spring Meeting & Exhibit, Phoenix, Arizona, April 17- 21 (2017).
5. Room Temperature Ferroelectricity and Photovoltaic Effect in Atomic Layer Deposited $SnTiO_X$ Thin Films. R. Agarwal, Y. Sharma, S. Chang, S. Nakhmanson, C. Takoudis, R. Katiyar, S. Hong, APS March Meeting, New Orleans, March 12-17 (2017).
6. Bulk photovoltaic effect in epitaxial (K, Nb) substituted BiFeO3 thin films. Radhe Agarwal, Fan Zheng, Yogesh Sharma, Seungbum Hong, Andrew M. Rappe and Ram S. Katiyar, 2017 APS March Meeting, New Orleans, March 12-17
7. Photoferroelectric and photovoltaic effects in ALD grown SnTiOx thin films. Radhe Agarwal, Yogesh Sharma, Siliang Chang, Serge Nakhmanson, Christos Takoudis, Ram S. Katiyar, and Seungbum Hong. 2017 APS March Meeting, New Orleans, March 12-17
8. Dielectric Relaxation in (BiFeO3)1-x-(KNbO3)x solid solutions, Radhe Agarwal, Fan Zheng, Yogesh Sharma, Andrew M. Rappe and Ram S. Katiyar, 2017 APS March Meeting, New Orleans, March 12-17
9. Effect of Off-Center Ion Substitution in Morphotropic Composition Lead Zirconate Titanate, Mohan Bhattarai, Shojan Pavunny, Alvaro Instan, James Scott, Ram Katiyar, 2017 MRS Spring Meeting & Exhibit, Phoenix, Arizona, April 17- 21
10. Ferroelectric Domain Structure and Photovoltaic Effect in Flexible BiFeO3 Films. Radhe Agarwal, Yogesh Sharma, Seungbum Hong, Ram Katiyar, 2017 MRS Spring Meeting & Exhibit, Phoenix, Arizona, April 17- 21
11. Probing the Tip Induced Polarization Switching and Magnetoelectric Coupling in PFN/NZFO/PFN Heteterostructure at Room Temperature. Dhiren Pradhan, Shalini Kumari, Rama Vasudevan, Aswini Pradhan, Sergei Kalinin, Ram Katiyar, 2017 MRS Spring Meeting & Exhibit, Phoenix, Arizona, April 17- 21
12. Multifunctional Properties of Highly c-Axis Oriented NZFO Thin Films. Dhiren Pradhan, Shalini Kumari, Aswini Pradhan, Ram Katiyar, 2017 MRS Spring Meeting & Exhibit, Phoenix, Arizona, April 17- 21
13. Science and Technology of Interface-Engineered BiFeO3/SrTiO3/BiFeO3 Nanolaminates with High Piezoelectricity and Low Leakage for Multifunctional and Biomedical MEMS/NEMS Devices. Orlando Auciello, Geunhee Lee, Erika Fuentes-Fernandez, Guoda Lian, Ram Katiyar, 2017 MRS Spring Meeting & Exhibit, Phoenix, Arizona, April 17- 21

<u>Graduate students in the area of Multiferroics (2016-2020):</u>

1. Danilo Barrionuevo (2016)
2 Dhiren Pradhan (2016)
3. Shalini Kumari (2016)
4. Yogesh Sharma (2016)
5. Radhe Agrawal (2017)
6. Alvaro Instan (2018)
7. Mohan Bhattarai (in progress)
8. Sita Dugu (in progress)