

Structural and magnetoelectric studies on $\text{Sr}_2\text{Fe}_{1-x}\text{Mn}_x\text{MoO}_6$ ($x=0.0, 0.25, 0.50$)

P.P. Jasnamol, P. Neenu Lekshmi, Manoj Raama Varma and Nandakumar Kalarikkal

Abstract — The present work investigates structural and magnetoelectric properties of $\text{Sr}_2\text{Fe}_{1-x}\text{Mn}_x\text{MoO}_6$ ($x= 0.0, 0.25, 0.50$) series of double perovskite for various potential applications. The $\text{Sr}_2\text{Fe}_{1-x}\text{Mn}_x\text{MoO}_6$ compounds were synthesized by solid state route with controlled reducing atmosphere ($\text{H}_2:\text{Ar}$) and characterized by means of XRD, SEM and FTIR. The XRD showed phase pure compound with tetragonal crystal structure. SEM images gave the single phase morphology and FTIR spectra showed two bands for $x=0.0$, three bands for $x= 0.25$ and four bands for $x=0.50$ compositions. The Cole Cole plot justified the presence of Mn^{2+} in the material enhancing the dielectric properties. The magnetoelectric characterization of $\text{Sr}_2\text{Fe}_{1-x}\text{Mn}_x\text{MoO}_6$ compounds are done and the ME coefficient α is increasing with Mn substitution.

Index Terms— Cole Cole, Double perovskites, FTIR, Magnetoelectric, Spintronics, $\text{Sr}_2\text{Fe}_{1-x}\text{Mn}_x\text{MoO}_6$.

1 INTRODUCTION

DOUBLE PEROVSKITE compounds of general formula $\text{A}_2\text{BB}'\text{O}_6$ (A- rare earth or alkaline earth ions and B, B'- transition metal ions) have been known for decades. Since large low-field tunneling type magnetoresistance (MR) at room temperature was found in an ordered double perovskite $\text{Sr}_2\text{FeMoO}_6$ [1], iron-based double perovskites such as $\text{Sr}_2\text{FeMoO}_6$ and $\text{Sr}_2\text{FeReO}_6$ have taken renewed attentions. Their ferrimagnetic Curie temperatures ($T_C \geq 400\text{K}$) are much higher than those of the colossal magnetoresistance (CMR) manganites, and the half-metallic nature was also predicted in the band calculations [2].

Advancement of technology demands extensive coexistence of ferroelectricity, ferroelasticity and ferromagnetism in a single compound or composite. In view of this, intensive research is being pursued in order to get multiferroic materials in which two or more ferroic properties coexist. Magnetoelectric (ME) coupling has become time-honored in magnetoelectric heterostructures [3], [4], [5], [6], which found a variety of applications in engineering devices, including spintronics [6], [7], [8], magnetoelectric sensors [9], [10], magnetoelectric flowmeters [11], spatial angular positioning devices [12], etc which are highly susceptible based on magnetic control of electric polarization or vice versa [10],[13]. For spintronic devices, highly magnetoelectric coupled materials are desirable in which the magnetic dipole and the electric dipole are mutually coupled.

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Further, magnetoelectrically coupled materials are promising candidates for low energy consumption miniaturized devices

wherein polarization or magnetization of the material can be externally controlled by applying a magnetic or electric field. The general pre-requisite for compounds to induce magnetoelectric coupling should be either antiferromagnetic or ferromagnetic and ferroelectric properties [14]. In Fe based ordered double perovskite A_2FeMO_6 (A=Ca, Sr, Ba; M= Mo, Re) compounds, Fe^{3+} ($3d^5$, $S=5/2$) and Mo^{5+} ($4d^1$, $S=1/2$) [or Re^{5+} ($5d^2$, $S=1$)] couple antiferromagnetically, whose conduction band is composed of the 4d (or 5d) down-spin electrons of Mo^{5+} (or Re^{5+}) [2]. When the Fe^{3+} ions are replaced by Mn^{2+} , the $\text{Sr}_2\text{MnMoO}_6$ shows insulating property as it contains no Mo 4d electrons responsible for metallic conductivity. Thus doping Mn on Fe site will provide the coexistence of electric and magnetic phases which may give rise to magnetoelectric (ME) effect, which is characterized by the magnetoelectric (ME) voltage coefficient, $\alpha=dE/dH$ [14].

2 EXPERIMENTAL DETAILS

The polycrystalline $\text{Sr}_2\text{Fe}_{1-x}\text{Mn}_x\text{MoO}_6$ ($x=0.0, 0.25, 0.50$) have been synthesized by standard solid state reaction technique with controlled reducing atmosphere. The raw materials SrCO_3 , Fe_2O_3 , MnCO_3 and MoO_3 (all are of high purity chemicals from Sigma Aldrich) were weighed stoichiometrically and mixed by hand in an agate mortar for 2 hours with distilled water as a medium. Then it was dried by keeping in hot air oven at 338K for one day. The precursor powders were calcined at 1473K for 4 hours in a stream of 5% H_2/Ar with a rate of 283K/minutes and allowed cool down naturally to room temperature. The calcined powders were pressed into pellets (diameter~11mm and thickness~1.5mm) and sintered at 1523K for 10 hours by following the same conditions. The crystal structure and phase purity of the powdered samples after sintering were characterized using a PANalytical X'Pert Pro Powder X-ray diffractometer (XRD) with a Ni filtered $\text{Cu K}\alpha$ radiation ($\lambda=1.5418 \text{ \AA}$). Scanning electron microscopy was carried out by using Carl Zeiss Scanning electron microscope. Infrared transmission spectra were obtained by using Perkin Elmer Spectrum Two IR Spectrometer.

The frequency dependent measurements were performed with HP-4192A LF Impedance Analyzer (Agilent) and magnetolectric coupling measurement was done by using Marine India measuring system.

3 RESULTS AND DISCUSSIONS

3.1 X-ray diffraction analysis and scanning electron microscopy

Fig. 1 shows the XRD patterns of the samples with varying x . It can be seen that the diffraction peak positions of $\text{Sr}_2\text{Fe}_{1-x}\text{Mn}_x\text{MoO}_6$ samples are the same for $x=0.0$, $x=0.25$ and $x=0.50$. All peaks in the XRD patterns are consistent with those of the pure $\text{Sr}_2\text{FeMoO}_6$ phase with tetragonal $I4/mmm$ crystal structure and are indexed according with Inorganic ICDD Pattern Reference code: 01-070-8133. It means that the Mn^{2+} is being substituted to the proper crystal structure.

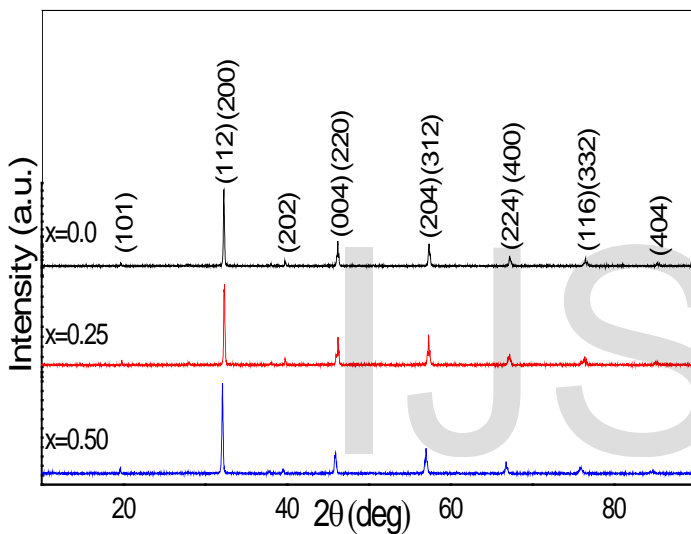


Fig.1. XRD patterns of $\text{Sr}_2\text{Fe}_{1-x}\text{Mn}_x\text{MoO}_6$.

Fig. 2 a), b) and c) show the scanning electron microscopy images of the sintered $\text{Sr}_2\text{Fe}_{1-x}\text{Mn}_x\text{MoO}_6$ with $x=0.0$, 0.25 and 0.50 respectively. Sintered pellets were broken into pieces to get the inside view and the images were recorded. One can observe the single phase crystals are formed and the grains are of micrometer size and are well packed inside the pellet form with maximum density. Such pellets are used for the dielectric and magneto electric coupling measurements.

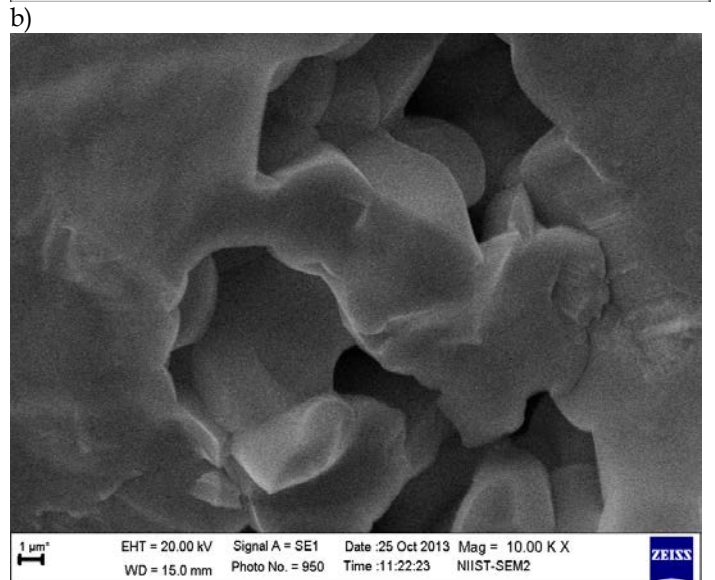
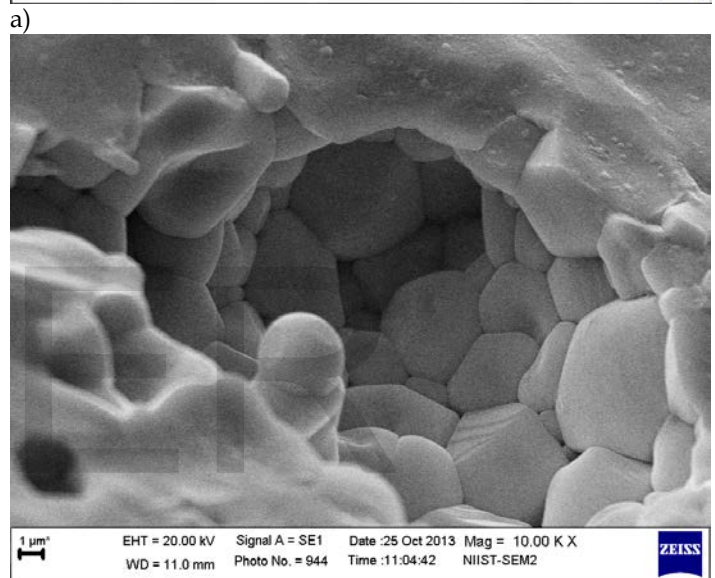
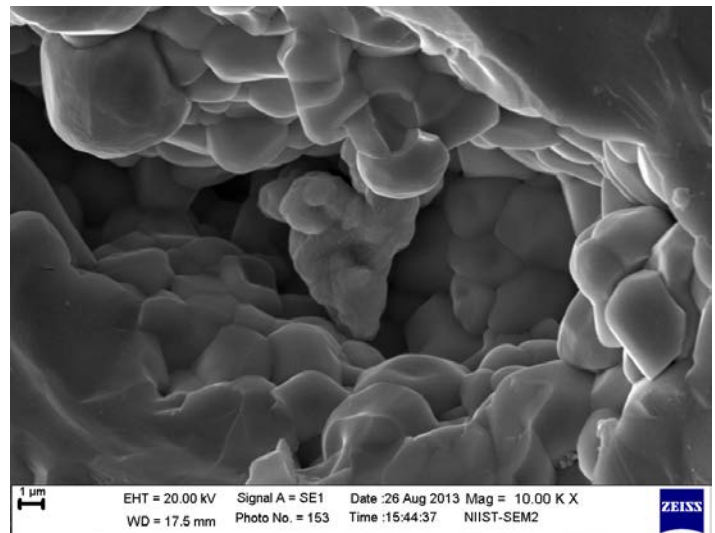


Fig.2. SEM images of $\text{Sr}_2\text{Fe}_{1-x}\text{Mn}_x\text{MoO}_6$ a) $x=0.0$; b) $x=0.25$; c) $x=0.50$ pellet sample.

3.2 Fourier Transform Infrared Spectroscopy

The FTIR transmission spectrum is taken by the samples embedded in KBr medium. Fig.3 shows IR spectra of the $\text{Sr}_2\text{Fe}_{1-x}\text{Mn}_x\text{MoO}_6$ powdered after sintering; in the spectral wavenumber range $1000\text{--}400\text{ cm}^{-1}$. The vertical black lines indicate the vibration bands. In according to the composition, the perovskite structure gave three characteristic vibration bands in FTIR spectrum between $850\text{--}400\text{ cm}^{-1}$, and is usually used for the perovskite phase identification [15]. The IR spectra of the double perovskite compounds $\text{Sr}_2\text{Fe}_{1-x}\text{Mn}_x\text{MoO}_6$ investigated in the present study (fig. 3) allow us to detect two bands for $x=0.0$, three bands for $x=0.25$ and four bands for $x=0.50$. The absorption band at $\sim 810\text{ cm}^{-1}$ is ascribed to Mo-O symmetric stretching mode and two at $\sim 620\text{ cm}^{-1}$ and $\sim 520\text{ cm}^{-1}$ are assigned to the anti-symmetric stretching mode of the MoO_6 octahedra, due to the higher charge of this cation [16], and is more evident for $x=0.50$ and $x=0.25$, since the presence of Mn^{2+} enhances the concentration of Mo^{6+} .

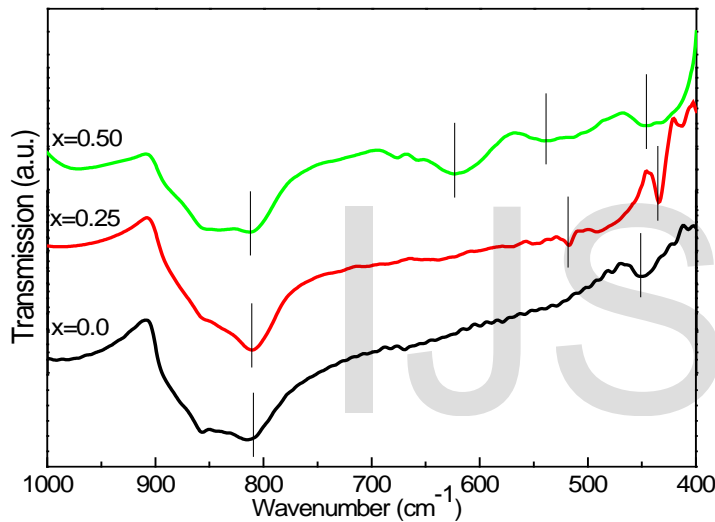


Fig.3 FTIR spectra of $\text{Sr}_2\text{Fe}_{1-x}\text{Mn}_x\text{MoO}_6$.

3.3 Dielectric and Magnetoelectric coupling measurements

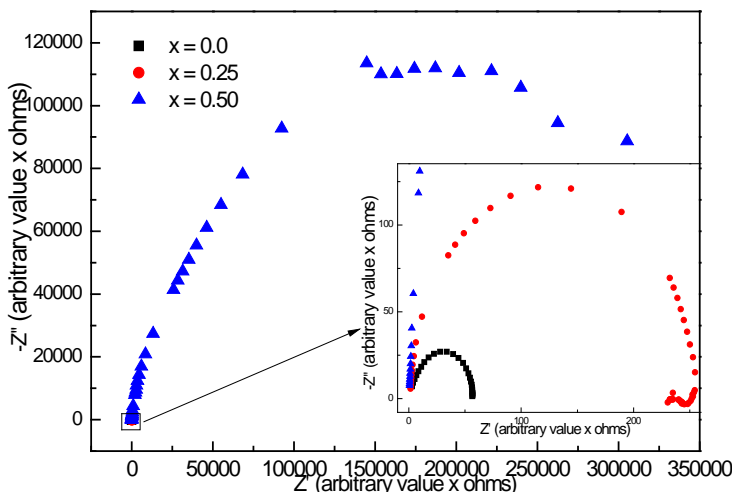


Fig.4 The cole-cole plot of $\text{Sr}_2\text{Fe}_{1-x}\text{Mn}_x\text{MoO}_6$.

The Cole-Cole plot (real part of impedance (Z') vs. negative of imaginary part of impedance ($-Z''$)) obtained with varying frequencies is plotted. One can see that the increasing in the radius of the semicircle obtained in cole-cole plot to a large extent as the percentage of Mn^{2+} is increased in the site of Fe^{3+} in $\text{Sr}_2\text{FeMoO}_6$ which justified the enhancement of insulating property of the half metallic or semi conducting natured material by Mn^{2+} substitution. The insight plot gives the magnified portion of rectangular marked region, which allows us to see the semi-circular graphs for $x=0.0$ and $x=0.25$ whose radius is much smaller compared to that of $x=0.50$.

The electric and the magnetic phases are existing in the $\text{Sr}_2\text{Fe}_{1-x}\text{Mn}_x\text{MoO}_6$ samples which lead to the effect called magnetoelectric coupling that can be characterized by means of magnetoelectric coupling coefficient, $\alpha=dE/dH$ [14], electrically as dP/dH and, or magnetically as dM/dH and is attributed as a measure of the easiness of the ME coupling [17]. Lock-in amplifier method has been chosen for the ME measurement of the particular pellets. A magnetic field is applied across the pellet and the corresponding ME output voltage is measured by the direct measurement of the the polarization (P) induced by the applied magnetic field (H). The sample holder is situated at the middle of a Helmholtz coil and is excited by the ac magnetic field H_{ac} established by the drive output of the tester. The electric dipoles within the pellet sample reorient themselves by the applied ac magnetic field, and causes an ac voltage drop on the top and bottom surfaces of the sample via ME coupling, which can be measured by utilizing the lock-in amplifier technique within the differential setting to dispose the induction voltage via the Faraday Effect. Thus the output voltage measured assures purely due to the ME coupling effect. For the case of DC bias magnetic field, an electromagnet is used to provide the field whose pole spacing is of 10mm [18], [19].

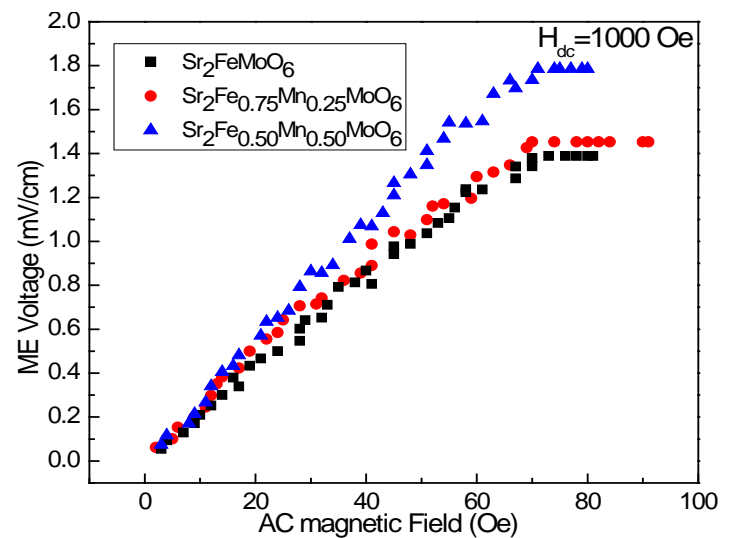


Fig.5 ME voltage vs. ac magnetic field with constant dc bias magnetic field.

The ac magnetic field (H_{ac}) dependence of ME voltage at room temperature is shown in Fig. 5. at a fixed frequency of 850 Hz

with constant dc bias field of 1000 Oe. The ME voltage increase with H_{ac} in a linear path upto 70 Oe and then remains constant. The value of α is determined from the slope of the ME voltage vs. H_{ac} below 70 Oe. The ME coupling coefficient obtained as $0.02584 \text{ mVcm}^{-1}\text{Oe}^{-1}$ for $x=0.50$ is higher than that obtained for $x=0.0$ ($\sim 0.01983 \text{ mVcm}^{-1}\text{Oe}^{-1}$) and for $x=0.25$ ($\sim 0.02015 \text{ mVcm}^{-1}\text{Oe}^{-1}$), which indicated an induced ME coupling in Mn^{2+} substituted compounds and it can be credited mainly due to the electric and magnetic interaction in the crystal lattice. Fig. 6 shows the ME coupling coefficient of the samples variation as a function of the dc bias magnetic field with fixed H_{ac} at 10 Oe, at room temperature. The maximum magnetoelectric coefficient is attained at optimized dc magnetic field [20]. In present study, no peaks are obtained in any composition and shows not much variation to the value as the applied DC magnetic field increase, so that one can conclude the inappreciable amount of geometrical frustration in the present samples, based on the symmetry concepts in perovskite structure. The origins regarding the room temperature ME effect might also be caused by the point defects [21] and in the present case this might be coming from the mixed valance of the B and B' cations in Mn^{2+} substituted $\text{Sr}_2\text{FeMoO}_6$.

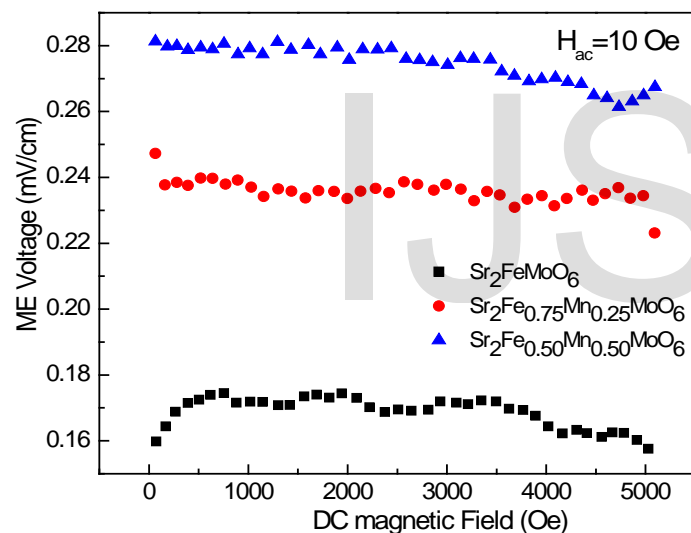


Fig.6 Variation of ME voltage as a function of the dc magnetic field.

4 CONCLUSION

A series of samples $\text{Sr}_2\text{Fe}_{1-x}\text{Mn}_x\text{MoO}_6$ with $x=0.0$, $x=0.25$ and $x=0.50$ were synthesized phase purely with tetragonal $I4/mmm$ crystal structure and obtained vibrational absorption bands corresponds to the composition. Frequency measurement showed a large increase in the dielectric properties with Mn^{2+} Substitution. Magnetoelectric coupling can be seen as increased by the presence of Mn^{2+} due to the abundance of dielectric phase embedded in the magnetic phase of $\text{Sr}_2\text{FeMoO}_6$ double perovskite and hence the work can be tuned with a promising state of the potential applications of magnetoelectric effect for the future engineering magnetoelectric devices.

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REFERENCES

- [1] K.-I. Kobayashi, T. Kimura, H. Sawada, K. Terakura, and Y. Tokura, "Room-temperature magnetoresistance in an oxide material with an ordered double-perovskite structure", *Nature*, 395, pp. 677-680, 1998.
- [2] K.-I. Kobayashi, T. Kimura, Y. Tomioka, H. Sawada, K. Tera-kura, and Y. Tokura, "Intergrain tunneling magnetoresistance in polycrystals of the ordered double perovskite $\text{Sr}_2\text{FeReO}_6$ ", *Physical Review B*, 59, pp. 11159-11162, 1999.
- [3] G. Bai, X. Gong, Z. G. Liu, Y. D. Xia, and J. Yin, "External stress enhanced magnetoelectric coupling in multiferroic heterostructures", *Journal of Applied Physics*, 112, pp. 114121- 114121-6, 2012.
- [4] M. Liu, O. Obi, J. Lou, S. Stoute, Z. Cai, K. Ziemer and N X Sun, "Strong Magnetoelectric coupling in Ferrite/ferroelectric multiferroic heterostructures derived by low temperature spin-spray deposition", *Journal of Physics D:Applied Physics*, 42, pp. 045007, 2009.
- [5] Mrittunjoy Guha Majumdar "Analysis of Stress-Coupled Magneto-Electric Effect in $\text{BaTiO}_3\text{-CoFe}_2\text{O}_4$ Composites using Raman Spectroscopy", *International Journal of Scientific & Engineering Research*, 3, pp. 1-7, 2012.
- [6] W. Kleemann, "Magnetoelectric Spintronics", *Journal of Applied Physics*, 114, pp. 027013, 2013.
- [7] T Fujita, M B A Jalil and S G Tan, "Multi-Channel spintronic transistor design based on magnetoelectric barriers and spin-orbital effects", *Journal of Physics: Condensed Matter*, 20, pp. 045205, 2008.
- [8] Tsymbal E. Y., "Spintronics: Electric toggling of magnets", *Nature Materials*, 11, pp. 12-13, 2011.
- [9] I. N. Soloviev, M. I. Bichurin, and R. V. Petrov, "Magnetoelectric Magnetic Field Sensors", *Progress In Electromagnetics Research Symposium Proceedings*, Moscow, Russia, August 19-23, pp. 1359-1362, 2012
- [10] Lage, E., Kirchof, C., Hrkac, V., Kienle, L., Jahns, R., Kno'chel, R., Quant, E. and Meyners, D. "Exchange biasing of magnetoelectric composites", *Nature Materials*, 11, pp. 523-529, 2012.
- [11] Vincent Cushing, "Magnetoelectric Flowmeter", *Review of Scientific Instruments*, 35, pp. 496-499, 1964.
- [12] D. T. Huong Giang, P. A. Duc, N. T. Ngoc, N. T. Hien, and N. H. Duc, "Spatial angular positioning device with three-dimensional magnetoelectric sensors", *Review of Scientific Instruments*, 83, pp. 095006-095006-6, 2012.
- [13] D N. Hur, S. Park, P.A. Sharma, J.S. Ahn, S. Guha and S. W. Cheong, "Electric Polarization reversal and memory in a multiferroic material by induced by magnetic fields", *Nature*, 429, pp. 392-395, 2004.
- [14] W. Eerenstein, N.D. Mathur, J.F. Scott, "Multiferroic and magnetoelectric materials", *Nature*, 442, pp. 759-765, 2006.
- [15] Mostafa, M. F., Ata-Allah, S. S., Youssef, A. A. A., Refai, H. S., " Electric and AC magnetic investigation of the manganites $\text{La}_{0.7}\text{Ca}_{0.3}\text{Mn}_{0.96}\text{In}_{0.04}\text{Al}_{(1-x)0.04}\text{O}_3$; ($0.0 < x < 1.0$)", *Journal of Magnetism and Magnetic Materials.*, 320, pp. 344-353, 2008.
- [16] Perianu, E. A., Gorodea, I. A., Gheorghiu, F., Sandu, A. V., Ianculescu, A.C., Sandu, I., Iordan, A.R., Palamaru, M. N., "Preparation and dielectric spectroscopy characterization of A_2MnMoO_6 (A=Ca, Sr and Ba) double perovskites", *Revista de Chimie (Bucharest)*, 62(1), pp.17-20, 2011.
- [17] Jungho Ryu, Shashank Priya, Kenji Uchino & Hyoun-EE Kim, "Magne-toelectric Effect in Composites of Magnetostriuctive and Piezoelectric Materials", *Journal of Electroceramics*, 8, pp. 107-119, 2002.
- [18] B. Raneesh, A. Saha and Nandakumar Kalarikkal, "Effect of gamma radiation on the structural, dielectric and magnetoelectric properties of nanostructured hexagonal YMnO_3 ", *Radiation Physics and Chemistry*, 89, pp. 28-32, 2013.

- [19] V.B. Naik, R. Mahendiran, "Magnetic and magnetoelectric studies in pure and cation doped BiFeO_3 ", *Solid State Communications*, 149, pp. 754-758, 2009.
- [20] Subhasis Roy, Ratnamala Chatterjee, S.B. Majumder, "Magnetoelectric coupling in sol-gel synthesized dilute magnetostrictive-piezoelectric composite thin films " *Journal of Applied Physics*, 110, pp. 036101-5, 2011.
- [21] Hyejin Ryu, P. Murugavel, J. H. Lee, S. C. Chae, T. W. Noh, Yoon Seok Oh, Hyung Jin Kim, Kee Hoon Kim, Jae Hyuck Jang, Miyoung Kim, C. Bae, and J.-G. Park "Magnetoelectric effects of nanoparticulate $\text{Pb}(\text{Zr}_{0.52}\text{Ti}_{0.48})\text{O}_3 - \text{NiFe}_2\text{O}_4$ composite films", *Applied Physics Letters*, 89, pp. 102907-102907-3, 2006.

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