Progress Report

Project Title: *"Functional Ceramics Ferroelectromagnetic Materials in Single Phase Solid Solutions"*

Proposed Goals in the original proposal:

1. We had proposed to do the detailed studies on magneto-dielectric effect in the ferroelectric ferromagnet (FEM) ternary oxide solid solutions like $Bi(TM)O_3$-$(La_{1-x}RE_x)_{0.67}(Ba/Ca)_{0.33}MnO_3$-$BTiO_3$,where TM=transition metal, initially Fe, RE=Rare Earth and B= Ba, Pb.
2. To find suitable composition such that the ferroelectric and ferromagnetic properties are observable at or near room temperature.
3. To decrease the difference between the ferroelectric (T_{fe}) and ferromagnetic (T_N or T_c) transition temperatures by **modifying $BiFeO_3$.**
4. Enhancement of ferroelectromagnetic behavior in the **modified $BiFeO_3$.**

Introduction: In solid solutions we can decrease the temperature difference between the two transitions (T_{FE} and T_{FM}) by selecting suitable constituent materials. Since $BiFeO_3$ is reported to show weak ferroelectromagnetic behavior, the addition of $La_{1-x}Ba_xMnO_3$ was expected to enhance the magnetic properties. LaMnO3 is an antiferromagnetic insulator and have cubic perovskite structure. The doping with divalent ions in the lattice causes double exchange mechanism in Mn^{3+} and Mn^{4+} ions. As a result $La_{1-x}Ba_xMnO_3$ becomes highly ferromagnetic. $PbTiO_3$ is a well known highly resistive ferroelectric material expected to improve the resistivity of the solid solution.

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14. ABSTRACT **1.Perform a detailed study on magneto-dielectric effect in the ferroelectric ferromagnet (FEM) ternary oxide solid solutions like Bi(TM)O3-(La1-xREx)0.67(Ba/Ca)0.33MnO3-BTiO3,where TM=transition metal, initially Fe, RE=Rare Earth and B= Ba, Pb. 2.To find suitable composition such that the ferroelectric and ferromagnetic properties are observable at or near room temperature. 3.To decrease the difference between the ferroelectric (Tfe) and ferromagnetic (TN or Tc) transition temperatures by modifying BiFeO3, and 4.To enhance ferroelectromagnetic behavior in the modified BiFeO3. The details of the results and discussion are presented in the final report.**			
15. SUBJECT TERMS			

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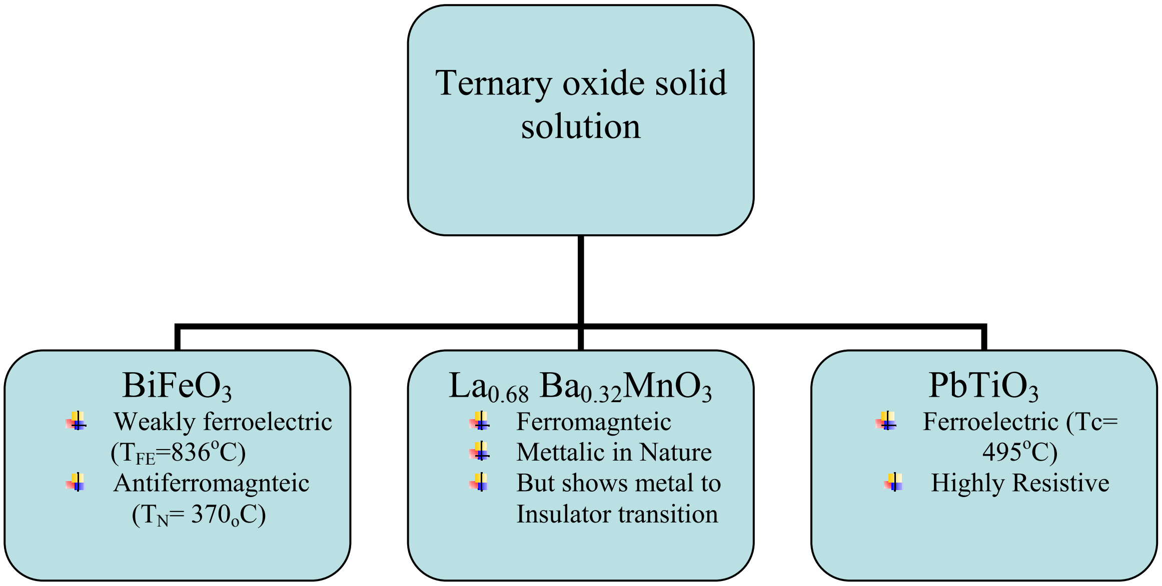


$(BiFeO_3)_{0.33}$-$(La_{0.68}Ba_{0.32}\ MnO_3)_{0.33}$-$(PbTiO_3)_{0.34}$ composition was selected for the preliminary studies. The samples were prepared by conventional solid-state route and characterized. But the results were not encouraging. *The <u>shortcomings</u> for these samples were found to be as follows:*

1. The dielectric losses in the sample were very high. Also, at higher temperatures the measurement of the dielectric constant became difficult due to low resistivity.
2. The sample has low resistivity, so the ferroelectric loop for the sample showed lossy behavior.
3. The M-H profile was showing the straight line passing through the origin, which is a direct indication of the paramagnetic or compensated antiferromagnetic behavior.
4. The resistivity decreases sharply with increase in the temperature.

Hence, to modify $BiFeO_3$, following three series of samples have been prepared and characterized to meet the abovementioned goals of project. The results are very good and encouraging.

Total number of manuscripts being prepared for sending for publications (based on the material discussed below) - 3.

Series of Modified $BiFeO_3$ prepared:

A. The solid solutions of $[(BiFeO_3)_x$-$(LaFeO_3)_{1-x}]_{1-y}$-$[PbTiO_3]_y$, where x= 0.50 and y=0.34, 0.40, 0.50, 0.60 and 0.70

B. The solid solutions of $[(BiFeO_3)_x$-$(BiMg_{0.5}Zr_{0.5}O_3)_{1-x}]_{0.45}$-$[PbTiO_3]_{0.55}$, where y= 0.30,0.35,0.40,0.45, 0.50

C. The solid solutions of $(LaFeO_3)_x$-$(PbTiO_3)_{1-x}$, where x= 0.10, 0.20, 0.30, 0.40, 0.67. (work is still going on)

Details of the experimental results have been discussed below.

A. The solid solutions of $[(BiFeO_3)_x$-$(LaFeO3)_{1-x}]_{1-y}$-$[PbTiO_3]_y$, where x= 0.50 and y=0.34, 0.40,0.50,0.60,0.70

Introduction: $BiFeO_3$ (BF) solid solutions with perovskite structure, has been a subject of extensive studies in recent years. $BiFeO_3$, with Fe^{3+} ions, is antiferromagnetic (T_N=370°C) and is also known to show ferroelectric behavior (T_c = 836°C). In BF, Bi ion with 2 electrons on 6s orbital move away from centrosymmetric position in its oxygen surroundings, giving rise to ferroelectricity. Since the ferroelectric and ferromagnetic orders in BF are associated with different ions, the two transition temperatures are far away from each other; and thus the magnetoelectric coupling in $BiFeO_3$ is very weak. However, if the polarization could be introduced in the system by a complex lattice distortion, by introducing substituents, ferroelectricity could be enhanced. This has lead to research in solid solutions like x ($BiFeO_3$)-(1-x) ($PbTiO_3$) (BF-PT), $BiFeO_3$-$BaTiO_3$, $BiFeO_3$- Pb(FeNb)O_3, $BiFeO_3$-$ReFeO_3$-$BaTiO_3$.Mainly the aim of the researchers, have been to improve the ferroelectric and magnetic properties of BF along with improved coupling.

The lattice structure of BF is a rhombohedrally distorted perovskite with space group R3C and the unit cell parameters are a = 2.96 Ǻ, $\alpha = 60^o$ and corresponding hexagonal unit cell parameters a=5.58 Å and c =13.9 Å. BF-PT solid solution has been reported to exhibit rhombohedral to tetragonal MPB at 70: 30. On the other hand the MPB of (BF_{1-x}- LF_{x})- (PT) is reported to be at 45:55. Recently, Cheng et al's results on 0.45 (BF_{1-x}- LF_{x})- 0.55(PT) with x= 0.1, 0.2, 0.3, demonstrate that c/a ratio decreases with increase of La content along with the improvement of magnetic and ferroelectric properties of the modified BF. Li et al also reported that the doping of La helps in grain growth, decreases the dielectric losses and improves the magnetic properties. Few things that are not addressed yet in literature are; (i) if the content of La is increased further, whether the dielectric and magnetic properties are improved further and whether this would shift the MPB of the BF-LF-Pt system (ii) The contribution of grain and grain boundaries to the ferroelectric properties in the multicomponent system (iii)

Synthesis:

The solid solutions were prepared using conventional solid-state reaction route. The raw materials of 99.9% purity (Aldrich) (Bi_2O_3, La_2O_3, PbO, Fe_2O_3, TiO_2) were weighed in a stochiometirc proportion and ball milled in acetone medium for 24 hours. The mixture was then calcined at 950^oC for 4 hours. Poly Vinyl alcohol (PVA) was mixed with these calcined powders then pressed into the form of small (1mm X 12mm) discs with hydraulic press. Discs were sintered at the $1100^{O}C$ for 2 hours in a lead rich environment.

Characterizations:

1. **X-ray diffraction** patterns were taken (Philips XRD) for the phase identification.
2. **Dielectric measurements** were observed with the impedance analyzer (HP 4192A). The Dielectric constant vs. temperature and dielectric constant vs. frequency profiles were taken.
3. **Ferroelectric Measurements** (P-E loop) were done with the ferroelectric tester (Radiant Technologies's Premier Precision II).
4. **Magnetic Measurements** were taken with the vibrating sample magnetometer (VSM). Both M-H and M-T profiles were studied.

Results and discussions:

In fig. 1 XRD patterns are shown for sintered samples of all compositions. The samples y=0.34, 0.40, 0.50 have cubic structure with the lattice parameters a= 3.183 Å, 3.189 Å and 3.95Å respectively whereas the sample y= 0.60 has the tetragonal structure with lattice parameters a=3.175 Å c=3.226 Å.

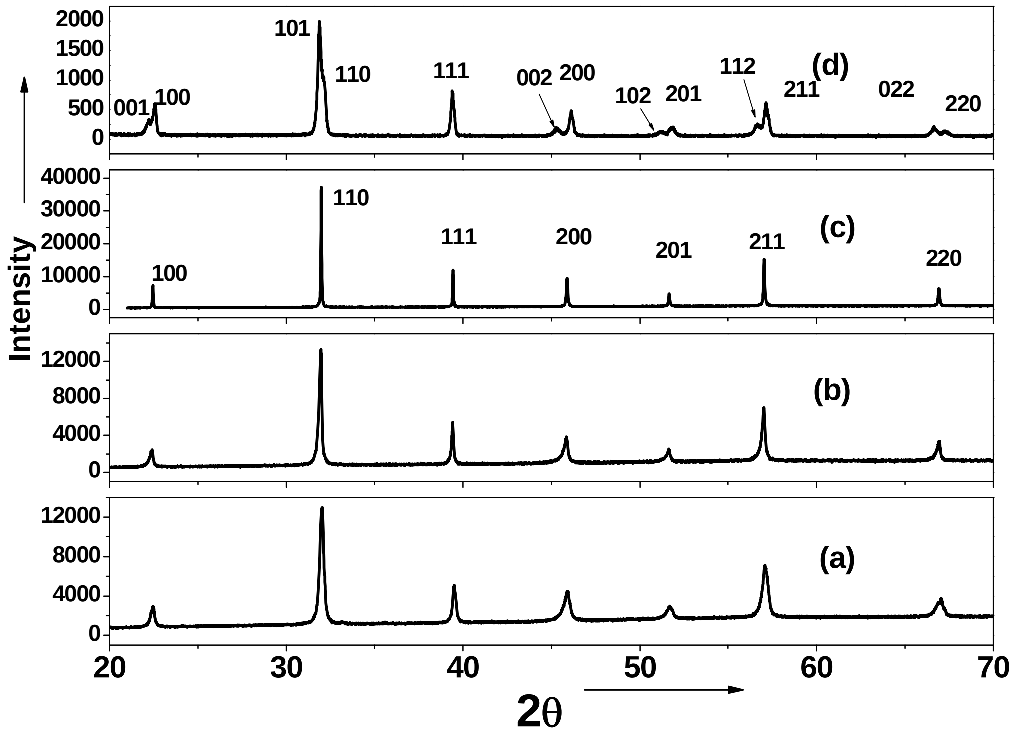


Fig.1. XRD patterns of the sintered samples of all the samples (a) For y=0.34 (b) y=0.40 (c) y=0.50 (d) 0.60

In fig. 2 dielectric constant vs. temperature profile has been given for the two extreme compositions of series i.e. y= 0.34 and y=0.60. In both of the samples the profiles are showing the relaxor behavior. The phase transitions are diffusive in nature and dipoles are relaxing near the transition temperatures.

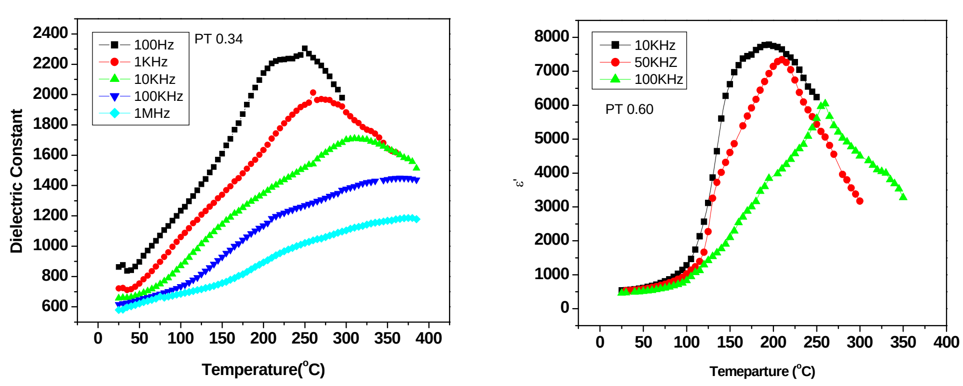


Fig.2. The dielectric constant vs. Temperature profile for the sample y=0.34 (100Hz-1MHz) and y=0.60 (10kHz- 100kHz)

In fig. 3 dielectric constant vs. frequency profile has been shown. The dielectric constant is decreases with increase in frequency, in all the samples. This is very normal behavior of the ferroelectrics.

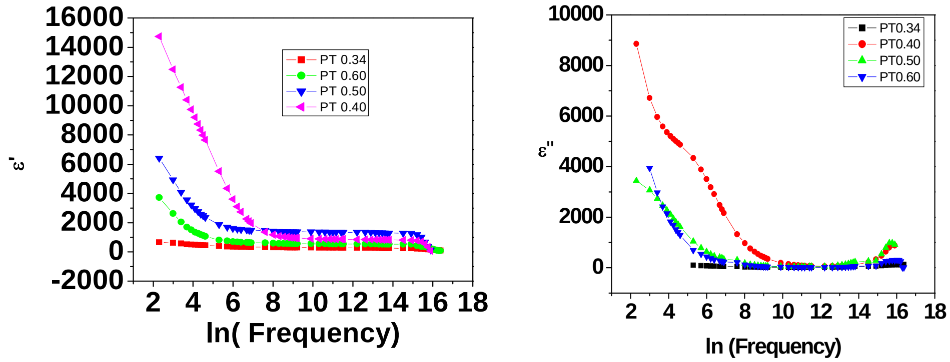


Fig 3. The variation of real part dielectric constant (ε') and imaginary part of dielectric constant (ε") with logarithmic frequency.

Cole-cole plots have been studied for all samples (In Fig.4). All samples have the contributions of grain and grain boundaries in the ferroelectric properties. First semi circle, which corresponds to the contribution of grains to the properties. The intercept of the semicircle on the real axis shifts towards the higher values of the dielectric constant (ε') as the content of $PbTiO_3$ increases up to y= 0.50. But for y= 0.60 the intercept again cuts the real axis at lower dielectric constant. This clearly indicates that as the phase changes from cubic to tetragonal the contribution of the grains become less. From y= 0.34 to y= 0.50 the radius of the semicircle is go on increasing, which indicates the more contribution in properties is due to the grains. But as the phase changes grain size also become less, which may be the cause of the less contribution from the grains. In the fig 5, the second semicircle shows the contribution of grain boundaries. The sample PT 0.50 shows a uniform semicircle and have less radius as compared to the other compositions. So from the above discussion, we conclude the PT 0.50

sample has uniform grain growth. Both grains and grain boundaries are contributing to ferroelectric properties.

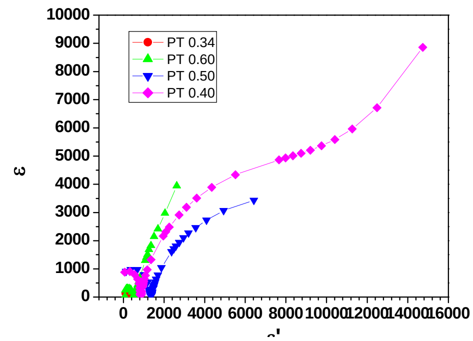


Fig.4 cole-cole plots for all samples at room temperatures.

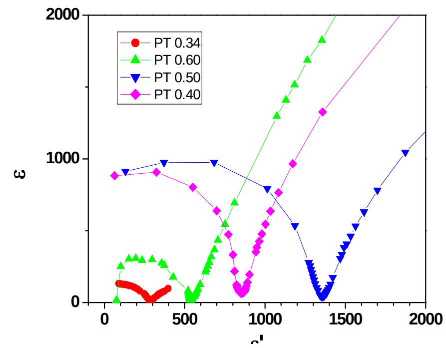
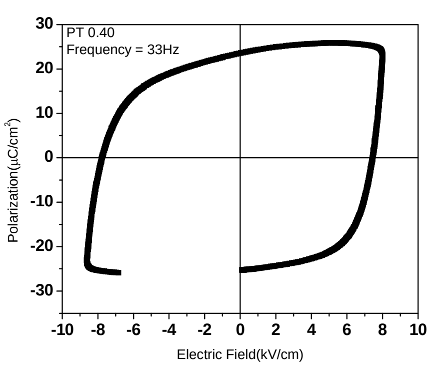
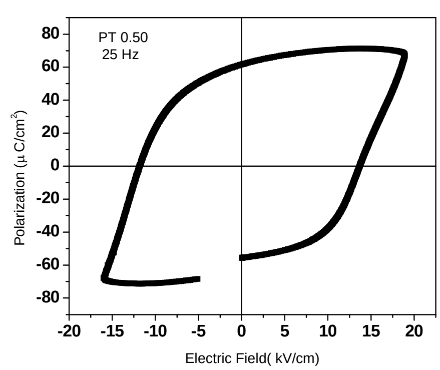


Fig. 5 enlarged portion of the first semicircle.

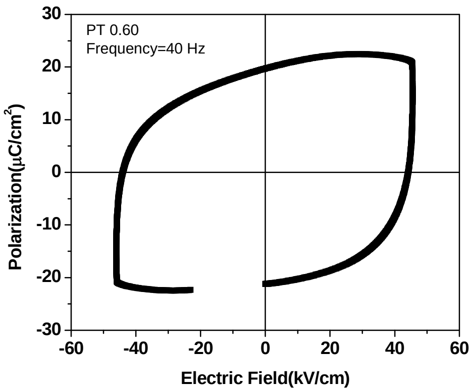
Ferroelectric loops for the samples have been shown in the fig. 6. The ferroelectric loops were taken at very low (different) frequencies ranges form 25Hz to 50 Hz. The ferroelectric loop for the sample y= 0.34 is a very lossy loop. The sample y= 0.50 has best ferroelectric loop in this series. The sample has larger P_r (~61.5 μC/ cm^2) value and low coercive field ~11.8 kV/cm. These values are very comparable to the values in the thin films till reported.



P-E loop for y=0.40 (33Hz) at room temperature



P-E loop for y=0.50 (25Hz) at room temperature



P-E loop for y=0.60 (40Hz) at room temperature

Fig. 6

The M-H Profiles are shown in the figure 7. All the samples are seems to be good ferromagnetic. The samples have good values of magnetic moment. With analysis of the arrot plots (In fig.8), frustrated magnetism has been confirmed in all samples. In the M-T profiles (fig.9) all the samples show two magnetic transitions at different temperatures. First transition is near the ~400°C, which very clear ferromagnetic like transition, and second transition is near the ~550°C. This clearly indicates two magnetic phases in the all samples.

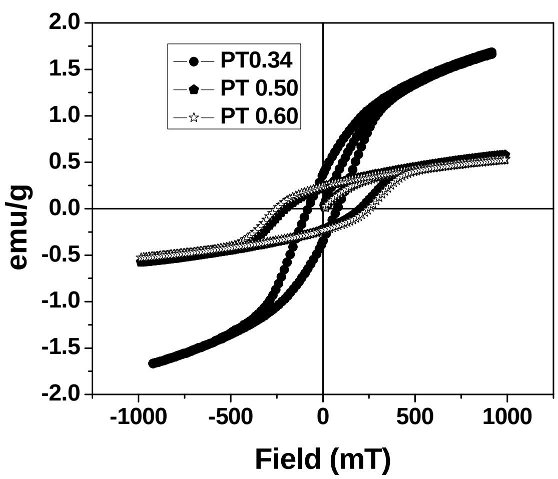


Fig.7 M-H plots for the samples y=0.34, y=0.50, y=0.60

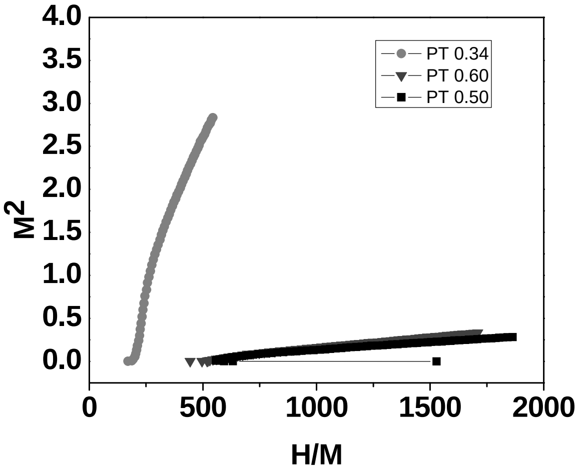


Fig. 8 M^2 vs. H /M (Arrot pots) for the samples y=0.34, y=0.50, y=0.60

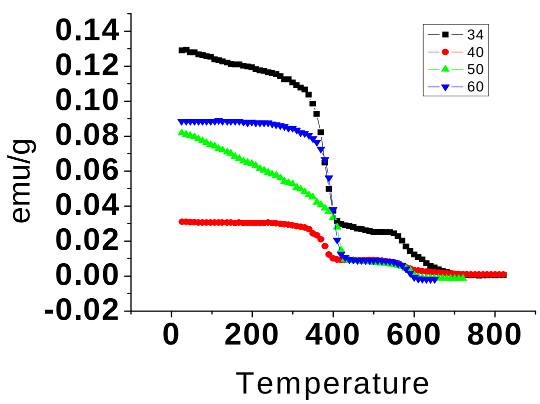


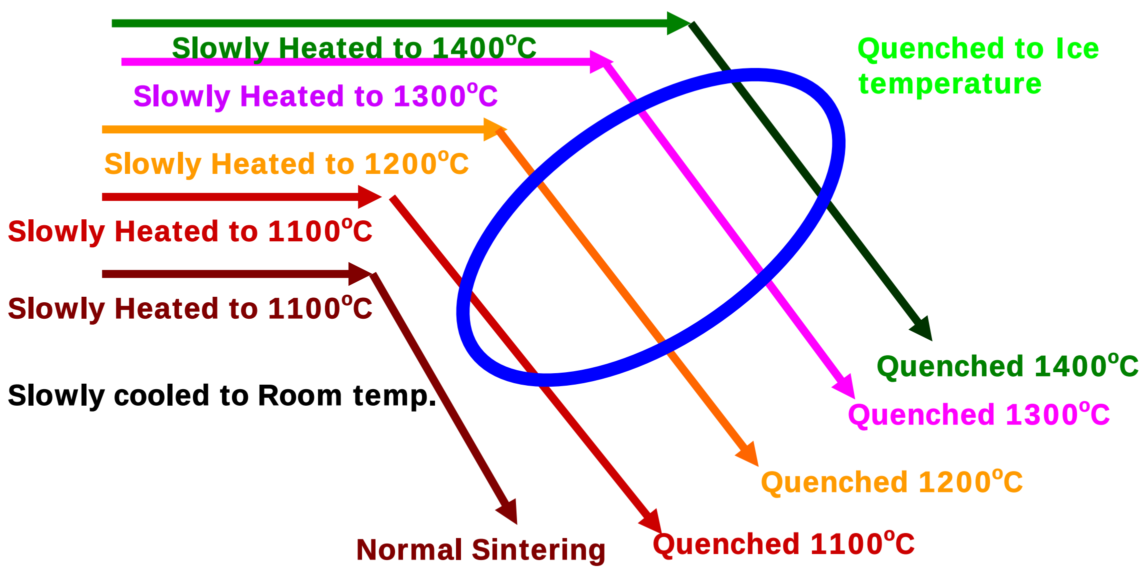
Fig.9 M-T profiles for all samples.

From the resistivity vs. electric field characteristics, it is clearly observed that with increase of the applied field, resistivity of sample decreases drastically and leakage current increases. The sample PT 0.50 has the maximum resistivity. Also it is noticed that beyond a particular field the application of the higher fields is not possible because the leakage current is too high to measure the polarization.

The dielectric constant follows the following trend PT 0.40> PT 0.50>PT 0.60> PT 0.34 and magnetic moment; PT 0.40< PT 0.50<PT 0.60< PT 0.34. From the above comparison, it is clear that in the multiferroic materials, one property enhances at the cost of the other. So the composition, which has largest dielectric constant value, has lowest magnetic moment So PT 0.50 is the composition, which is found to be best multiferroic in this series.

To Study the dependence of multiferroicity on the variation of microstructure the sample y= 0.34 is quenched at different temperatures. Tha samples were quenched to the ice-water from 1100^{o}C, 1200^{o}C, 1300^{o}C and 1400^{o}C.

Different heat treatments



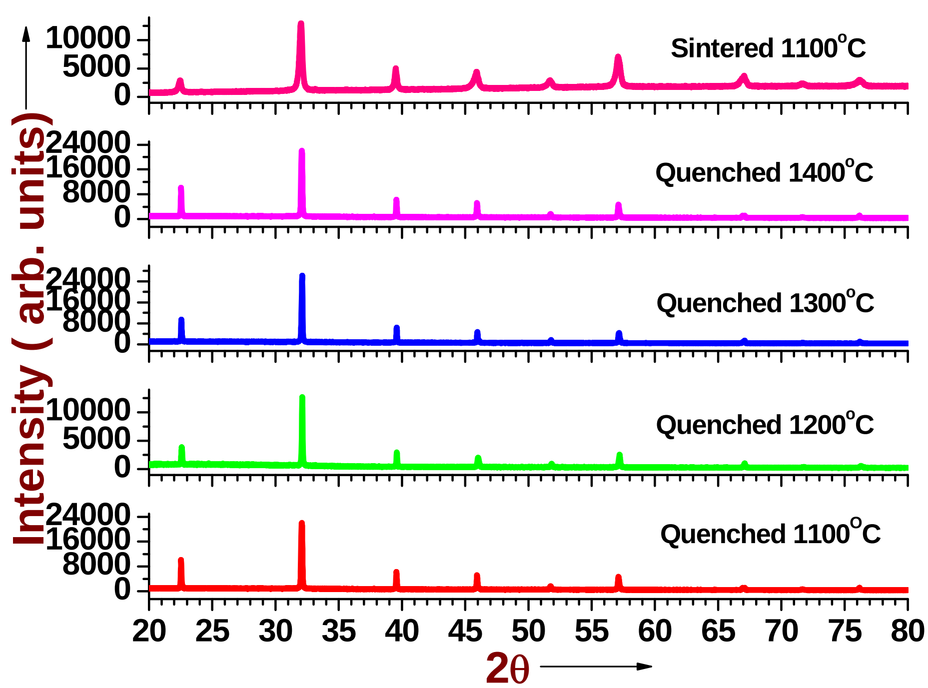
Characterizations:

1. **X-ray diffraction** patterns were taken (Philips XRD) for the phase identification.
2. **SEM microgrphs** were taken to analyze the surface morphology and grain size.
3. **EDAX**

4. **Dielectric measurements** were observed with the impedance analyzer (HP 4192A). The Dielectric constant vs. temperature and dielectric constant vs. frequency profiles were taken.
5. **Ferroelectric Measurements** (P-E loop) were done with the ferroelectric tester (Radiant Technologies's Premier Precision II).
6. **Magnetic Measurements** were taken with the vibrating sample magnetometer (VSM). Both M-H and M-T profiles were studied

Results and Discussions:

In the Fig. the XRD patterns have been shown. The sample y=0.34 have the cubic structure, in all quenched samples. There is no variation of lattice parameters are almost same in all the samples.



SEM micrographs clearly indicate the grain growth with the increase in temperature. There is drastic change in the grain size (~1μm to ~6 μm) as temperature increases from 1200°C to 1300°C. There are small particles, that was indicated in the SEM micrographs were analyzed by the EDAX. Which concludes that there some segregation of the second phase. This phase have the enrichment of Fe in the composition.

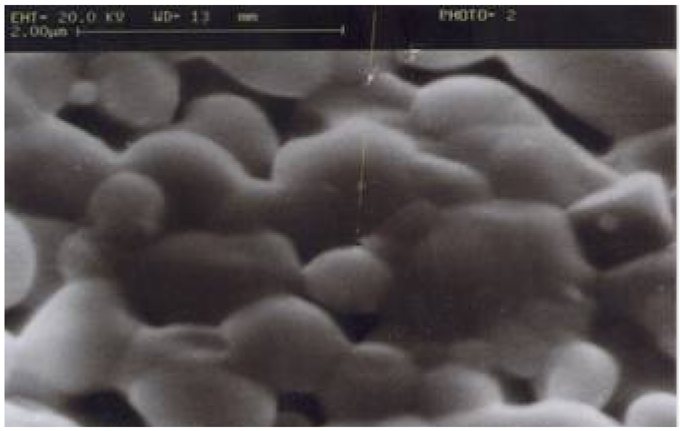
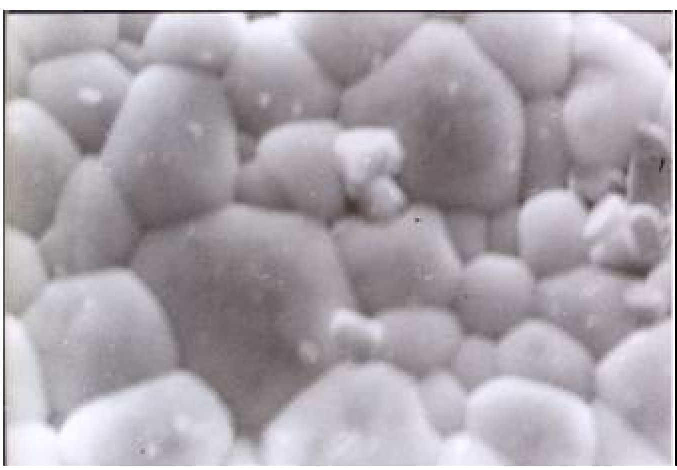
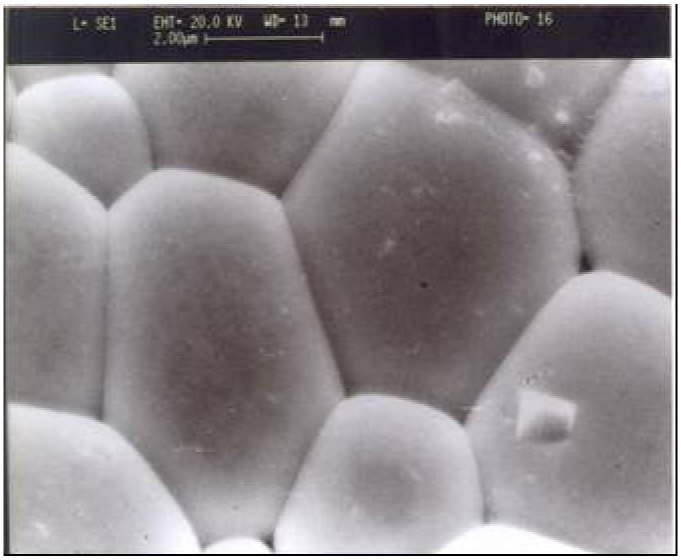


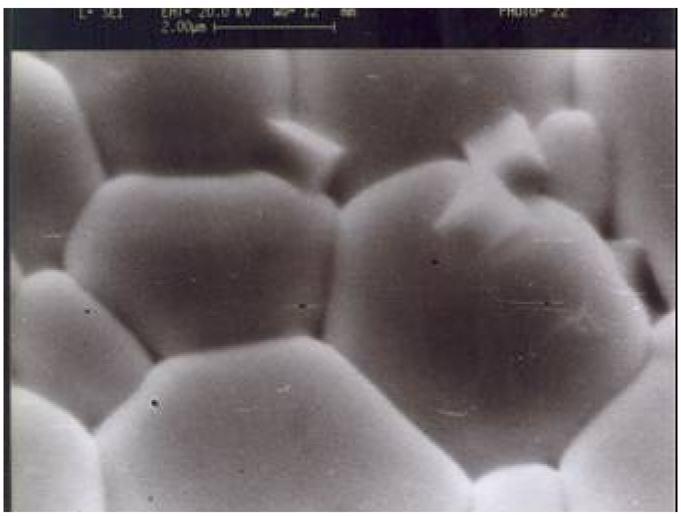
Fig SEM micrograph for the 1100oC quenched sample



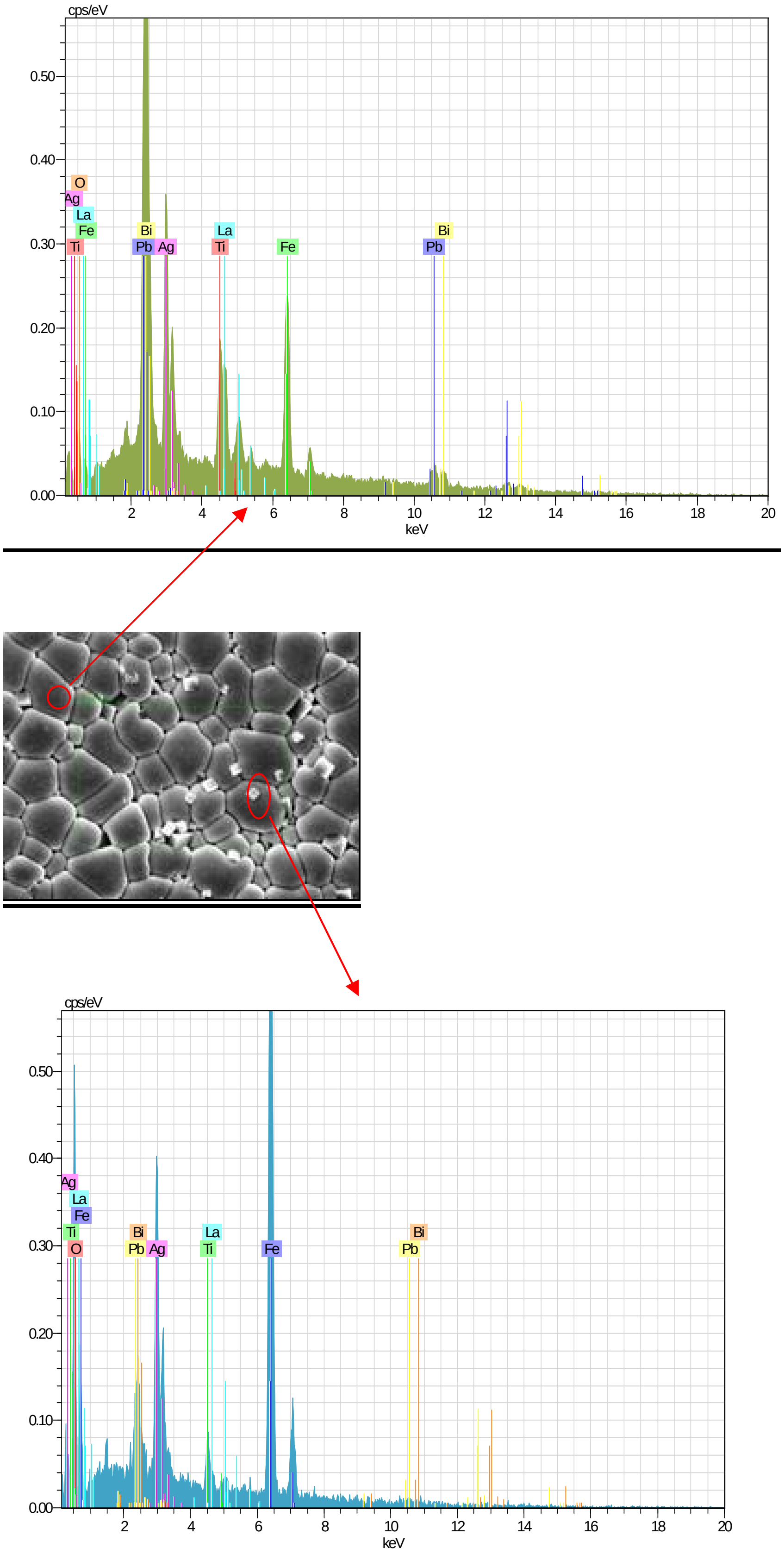
1200°C quenched sample



1300^{o}C quenched sample



1400^{o}C Quenched Sample


cps/eV
0.50
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0.30
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La
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keV
cps/eV
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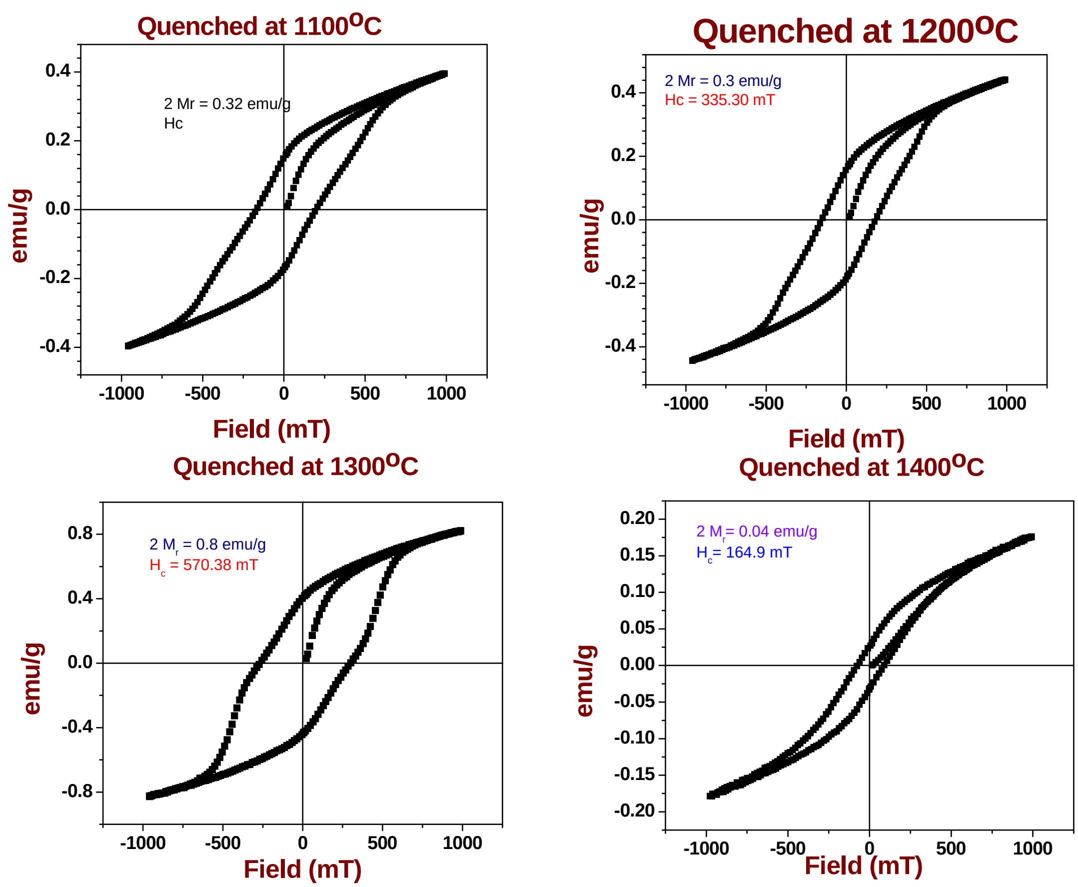
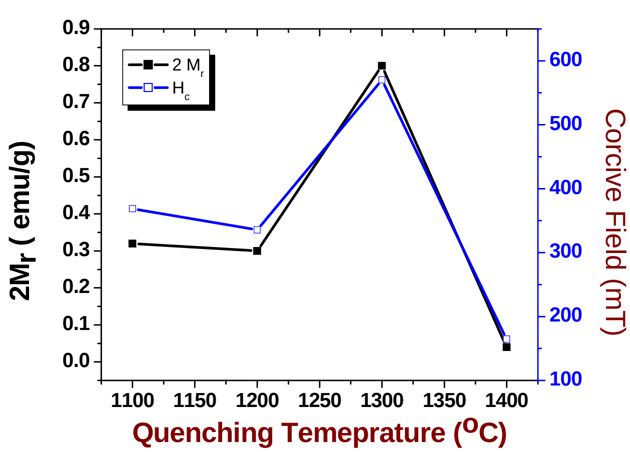
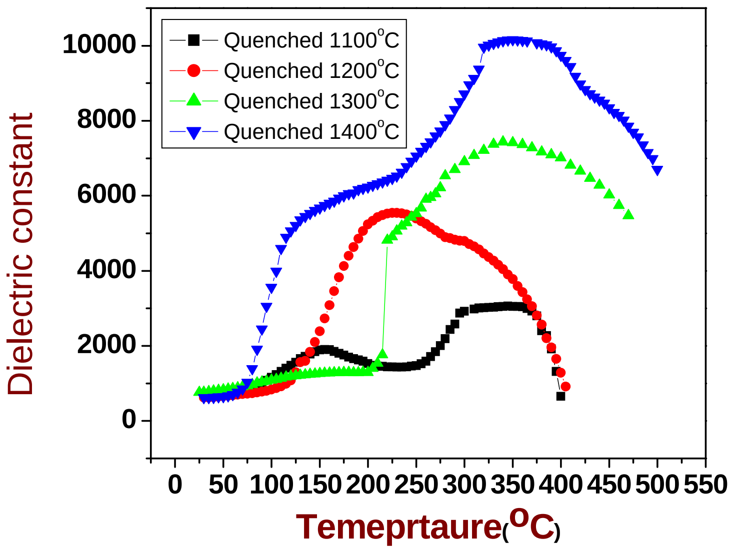
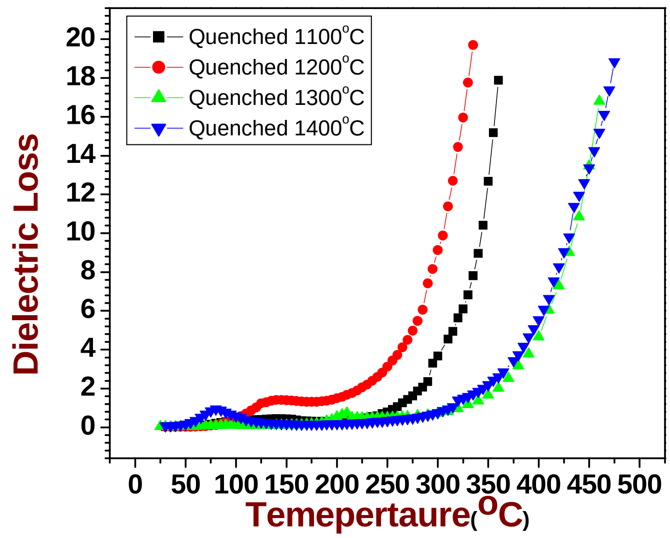

Quenched at 1100^{o}C
2 Mr = 0.32 emu/g
Hc
emu/g
Field (mT)
Quenched at 1200^{o}C
2 Mr = 0.3 emu/g
Hc = 335.30 mT
emu/g
Field (mT)
Quenched at 1300^{o}C
2 M_r = 0.8 emu/g
H_c = 570.38 mT
emu/g
Field (mT)
Quenched at 1400^{o}C
2 M_r= 0.04 emu/g
H_c= 164.9 mT
emu/g
Field (mT)


2 M_r
H_c
$2M_r$ (emu/g)
Corcive Field (mT)
Quenching Temeprature (^{O}C)

M-H profiles of the quenched samples are shown in the above figure. Quenched 1300°C has maximum retentivity (~0.4 emu/g) and the coercive field (~ 570 mT). May be due the large grains, the magnetic properties were enhanced in this sample. The magnetic properties change drastically in the 1400°C quenched sample.





In the above two figures, dielectric constant vs. temperature and dielectric loss vs. temperature plots for all the quenched samples has been shown. As the quenching temperature increases, dielectric constant also increases. But in all samples the ε′ vs. T profile show two anomalies.

B. The solid solutions of [$(BiFeO_3)_x$-($BiMg_{0.5}Zr_{0.5}O_3)_{1-x}]_{0.45}$-$[PbTiO_3]_{0.55}$, where y= 0.30,0.35,0.40,0.45, 0.50

Synthesis: The solid solutions were prepared using conventional solid-state reaction route. The raw materials of 99.9% purity (Aldrich) (Bi_2O_3, MgO, ZrO2, PbO, Fe_2O_3, TiO_2) were weighed in a stochiometirc proportion and ball milled in acetone medium for 24 hours.The mixture was then calcined at 850^{o}C for 2 hours. Poly Vinyl alcohol (PVA) was mixed with these calcined powders then pressed into the form of small (1mm X 12mm) discs with hydraulic press. Discs were sintered at the 1050^{O}C for 2 hours in a lead rich environment.

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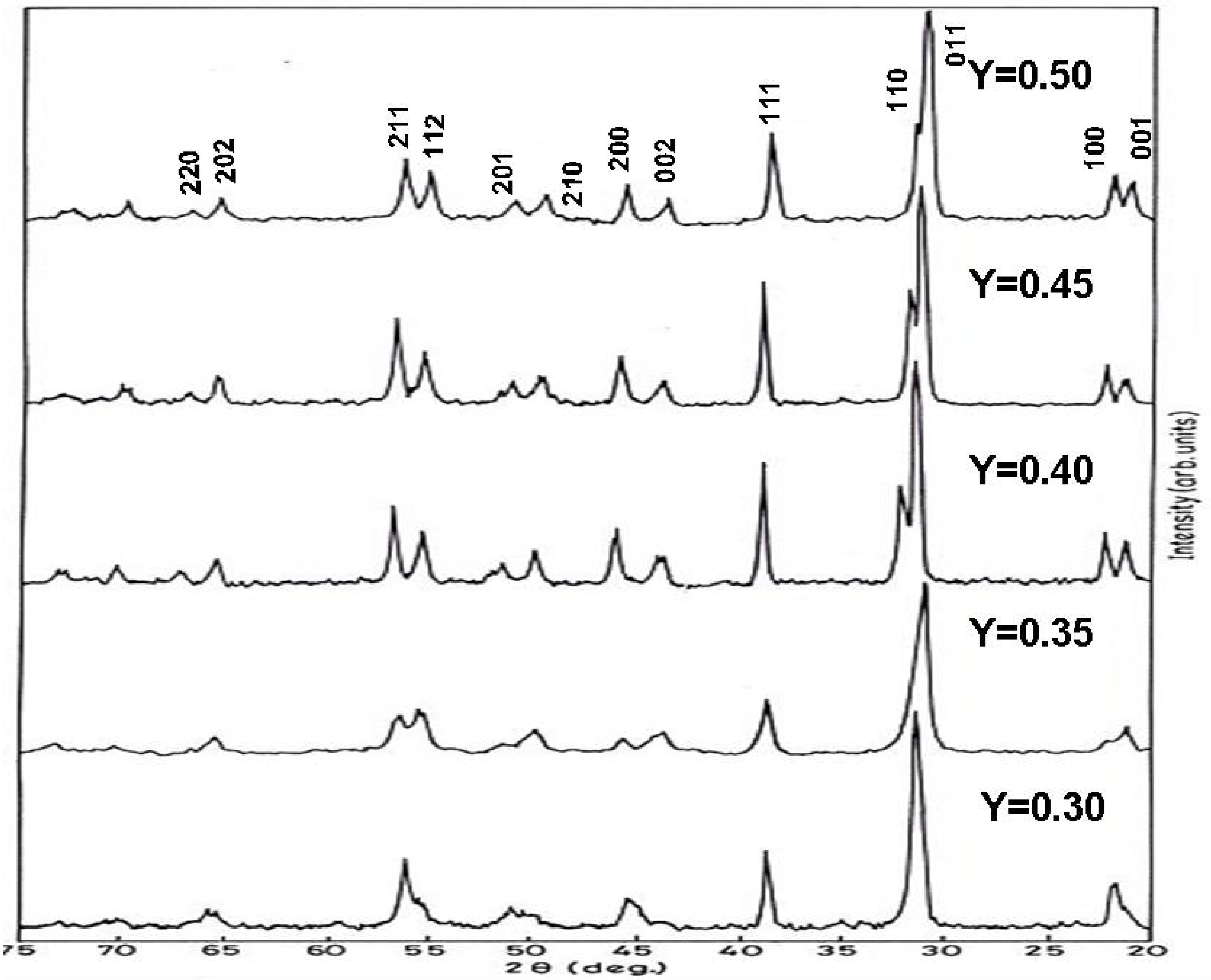
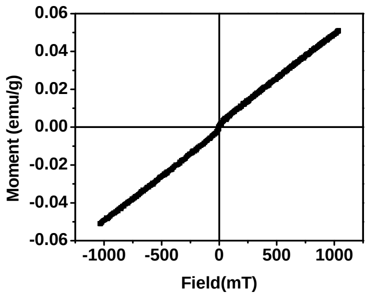
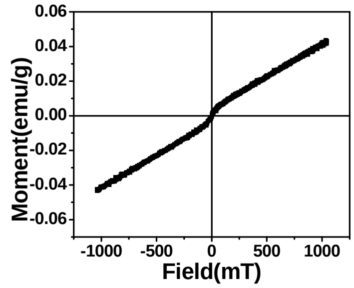
Results and Discussions:



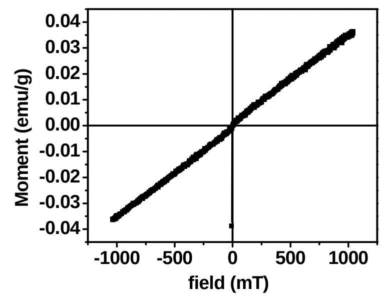
In the above figure the x-ray diffraction patterns of all the samples has been shown. All samples have tetragonal structure. The M-H profiles for the samples are shown in the figures below.



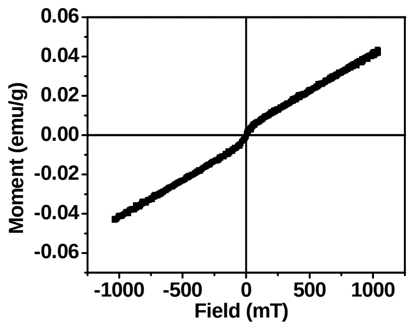
Y=0.30



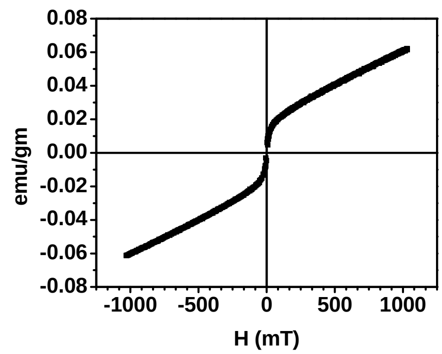
Y=0.35



Y=0.40

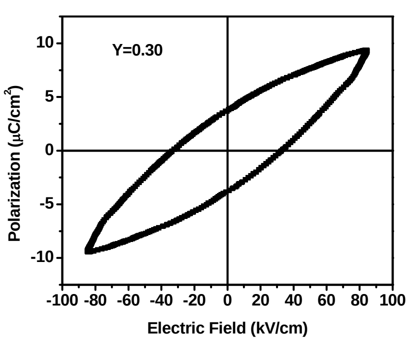


Y=0.45



Y=0.50

Ferroelectric loops at room temperature.



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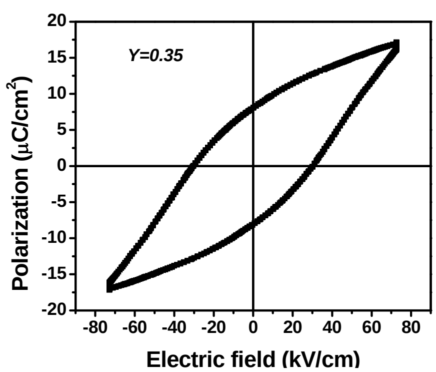

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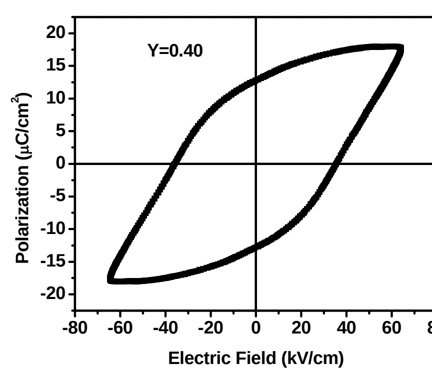

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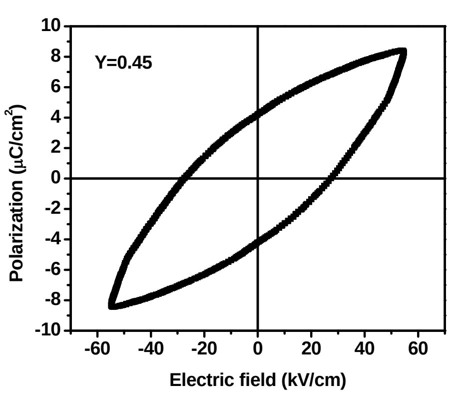

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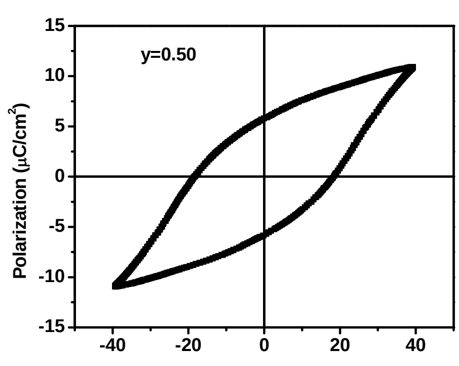

Y=0.50

C. **The solid solutions of $(LaFeO_3)_x$-$(PbTiO_3)_{1-x}$, where x= 0.10, 0.20, 0.30, 0.40, 0.67. (work is still going on)**

Introduction: Recently $BaTiO_3$ is doped with Ni and Co to get multiferroic properties. So the solid solutions of $(LaFeO_3)_x$–$(PbTiO_3)_{1-x}$ have been synthesized and characterized.

Synthesis:

The solid solutions were prepared using conventional solid-state reaction route. The raw materials of 99.9% purity (Aldrich) (Bi_2O_3, La_2O_3, PbO, Fe_2O_3, TiO_2) were weighed in a stochiometirc proportion and ball milled in acetone medium for 24 hours.The mixture was then calcined at 950^{o}C for 12 hours. Poly Vinyl alcohol (PVA) was mixed with these calcined powders then pressed into the form of small (1mm X 12mm) discs with hydraulic press. Discs were sintered at the 1250^{O}C for 6 hours in a lead rich environment.

Results and Discussion:

In this series the work is still going on. So the LF0.2-PT 0.8 sample has been synthesized and characterized. The ferroelectric and ferromagnetic properties of this sample are shown below.