Multiferroic Properties of Lanthanum, Samarium and Iron Doped Lead Titanate Solid Solutions

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Abstract
Multiferroic solid solutions of $(Pb_{1-x}La_{x/2}Sm_{x/2})(Ti_{1-x}Fe_x)O_3$ (where x = 0.1, 0.2, 0.3) are synthesized by conventional Solid State Reaction Route method. The samples are calcined at 950°C and sintered at 1200 °C for proper grains growth. The prepared samples are characterized to reveal the Structural, Optical and Magnetic properties. The structural analysis is done by XRD and FESEM techniques which show the formation of single phase material and proper grain growth. Raman Spectroscopy shows shifting of chemical bonding and confirmation of phase as the doping of Lanthanum, Samarium and Iron is increased. The magnetic properties are studied by Vibrating Sample Magnetometer which shows the characteristic phenomenon as doping of magnetic ion is increased.

Keywords
Multiferroics, Ferroelectric ($PbTiO_3$), Ferromagnetism, Solid State Reaction Route.

I. Introduction
Multiferroic materials are the topic of great interest due to their advanced fundamental nature and technological importance point of view, where the two phenomenon of Ferromagnetism (FM) and Ferroelectricity (FE) co-exist simultaneously. Their wide applications in storage devices, spintronics and electro-optic devices have been reported in literature [1-3].
This type of behavior arises in perovskite materials ABO_3, where A-site shows ferroelectric nature due to lone pair electrons and B-site shows magnetic order, on combining both we get multiferroic phenomenon in a single phase material and fall under category of Type-I multiferroic materials.
Keeping this thing in mind various research groups are working on these types of materials. Room temperature multiferroic properties of single phase $BiFeO_3$ doped with lanthanum has been reported [4-5]. Addition of Lead Zirconate Titanate (PZT) to $BiFeO_3$-$PbTiO_3$ has been investigated and obtained significant decrease in Curie temperature as well as enhanced dielectric properties [6]. The multiferroic binary systems of $BiFeO_3$-$PbTiO_3$ and $SmFeO_3$-$PbTiO_3$ solid solutions have already been reported [7-8] and inspiration for the present work in this paper.
Here, we have prepared $(Pb_{1-x}La_{x/2}Sm_{x/2})(Ti_{1-x}Fe_x)O_3$ (where x = 0.1, 0.2, 0.3) solid solutions by solid state reaction route method. Lead Titanate is very interesting ferroelectric material due to its promising physical properties and high Curie temperature (Tc ~ 495°C). So we are substituting Pb^{2+} by La^{3+} and Sm^{3+} and Ti^{4+} by Fe^{3+} for stable stoichiometery of the system.

II. Experiment
The conventional solid state reaction route method is followed for preparing solid solutions. All the raw chemicals PbO, La_2O_3, Sm_2O_3, TiO_2 and Fe_2O_3 are of 99.9% pure Sigma Aldrich Company has been used. They are weighed in stoichiometric proportion and mixed in ball mill for 24 hours in propane-2-ol as a medium. The mixed powder is calcined at 950°C for 12 hours for the phase formation. Polyvinyl alcohol by 2 wt % is added to the resultant powder as a binder. Then, this powder is used to prepare small disks of approximate 10 mm diameter with the help of hydraulic press. Finally these disks are sintered at 1200°C for proper nucleation growth. The resultant sintered disks are then characterized using various techniques.

III. Results and Discussions
The room temperature x-ray diffraction patterns are obtained by using (Cu K_α radiation (λ = 1.540 A^0 Shimadzu MAXima XRD-7000) as shown in fig. 1.

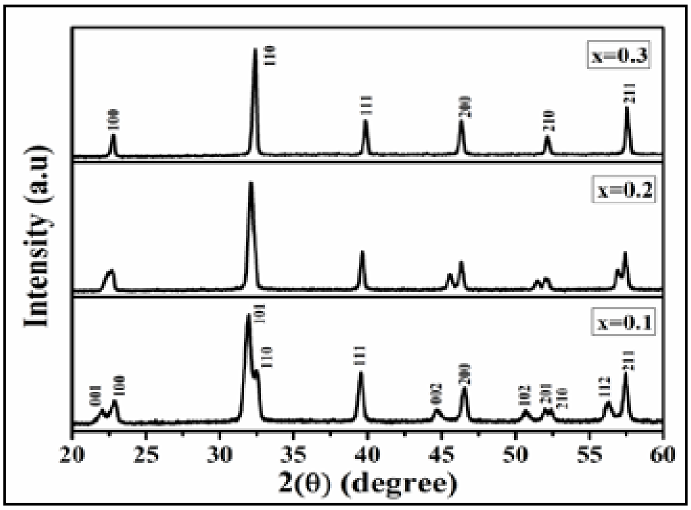

Fig. 1: The XRD Patterns of Prepared $(Pb_{1-x}La_{x/2}Sm_{x/2})(Ti_{1-x}Fe_x)O_3$ for x = 0.1, 0.2, 0.3.

As clear from the figure single phase tetragonal structure (P4mm space group) is obtained for x = 0.1 with splitting of (100), (110), (200), (210) and (211) peaks. As the doping of lanthanum, samarium and iron increases in $PbTiO_3$, its tetragonality decreases for x = 0.2 and we get cubic structure for x = 0.3 composition.
FESEM micrograph (taken by Carl Zeiss Supra 55) reveals surface morphology of the samples as shown in fig. 2.
It is clear from micrographs as doping of La^{3+}, Sm^{3+} and Fe^{3+} ions increases on A-site and B-site of $PbTiO_3$, density and grain size increases for x = 0.2 composition as shown in fig. (b) and cubic grains growth appeared for sample (c) x = 0.3 which is in agreement with XRD.
Energy Dispersive X-Ray Analysis (EDAX) (50 mm^2 Oxford Instrument attached with FESEM) is performed to confirm the elements and their wt% in each sample shown alongwith micrographs and Table 1.

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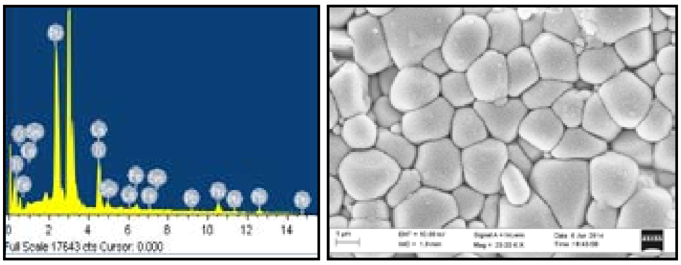
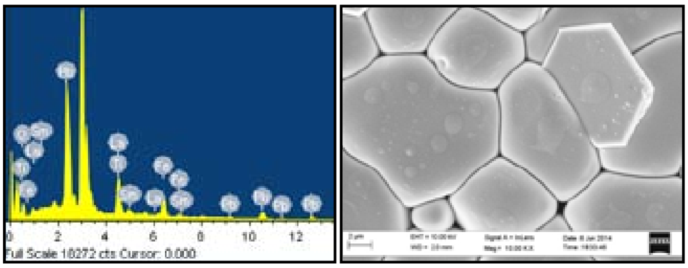


2(a)



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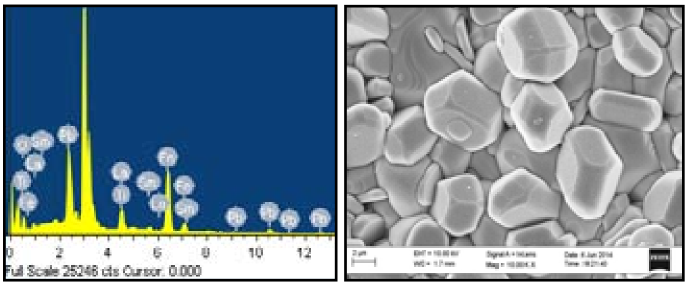

2(c)

Fig. 2: The FESEM micrograph and EDAX of (Pb_{1-x} $La_{x/2}Sm_{x/2}$) ($Ti_{1-x}Fe_x$) O_3 for (a) x = 0.1(b) x = 0.2 and (c) x = 0.3.

Table 1: Elemental Compositions in Weight% Evaluated by EDAX Analysis

Elements	x = 0.1 (Wt %)	x = 0.2 (Wt %)	x = 0.3 (Wt %)
Pb	66.19	56.69	38.45
Sm	2.40	4.04	4.85
La	2.60	4.28	3.68
Fe	2.68	10.41	35.99
Ti	15.39	13.08	7.01
O	10.74	11.49	10.02

Raman spectroscopy of all sintered sample is done (by RENISHAW inVia Raman Microscope, using laser of 488 nm with power of 50% and exposure time of 90 sec) in order to confirm the phase development in $PbTiO_3$ with doping. The room temperature Raman spectra obtained for x = 0.1 shows most of phonon modes allowed in tetragonal phase that are E (1TO), E(1LO), A1(TO), E(2T0), B1+E, A1(2TO), E(2LO), E(3TO), A1(3TO) and E(3LO) . Also it has been reported that for tetragonal phase T_{1u} mode splits into two modes transforming as A1+E and T_{2u} mode also split into two modes transforming as B1+E. All these modes are Raman active. Whereas in cubic phase optical phonon modes transform as $3T_{1u}+T_{2u}$ irreducible transformation in which T1u mode is infrared active and T2u mode is silent that is neither infrared nor Raman active [9].This is in agreement with composition x = 0.2 and x = 0.3 as doping increases structure changes from tetragonal to cubic phase due to which there is slight shifting in Raman active bands which appear to be broad and almost disappear for x = 0.3 composition as shown in fig. 3.

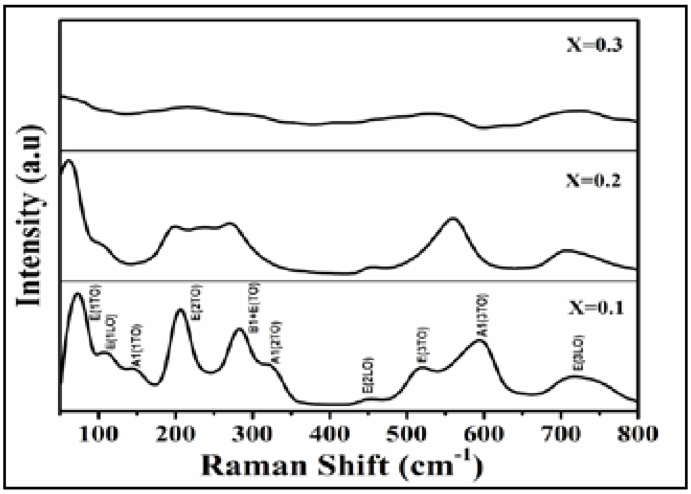

Fig. 3: Raman Spectra of Doped $PbTiO_3$ for x = 0.1, 0.2 and 0.3.

Magnetic study of the sintered samples is done by Vibrating Sample Magnetometer (named Microsense E29) technique and M-H curves are obtained as given below in fig. 4. The values of coercive Field, remanent magnetization and saturation is found to increase as the content of iron increased in x = 0.2 and x = 0.3 as shown in Table 2.

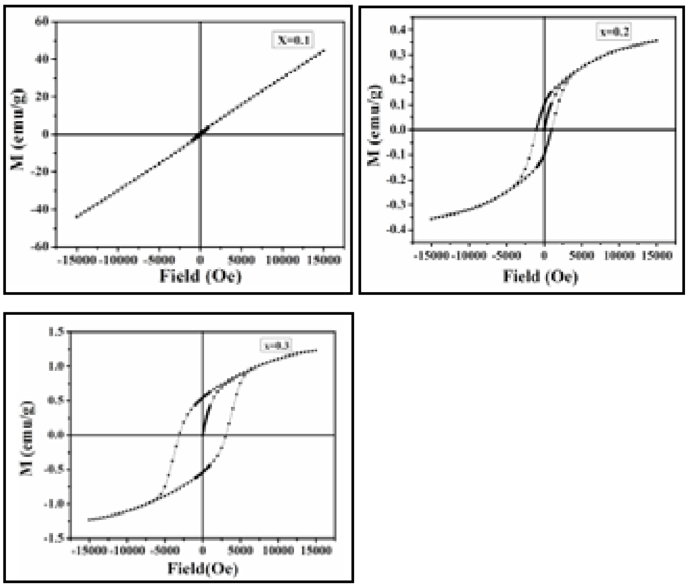

Fig. 4: Compositional Variation of M-H Curves for (Pb_{1-x} $La_{x/2}$ $Sm_{x/2}$) ($Ti_{1-x}Fe_x$) O_3 where x = 0.1, 0.2 and 0.3.

Table 2: Magnetic Parameters for ($Pb_{1-x}La_{x/2}Sm_{x/2}$) ($Ti_{1-x}Fe_x$) O_3 According to Compositions

Composition By mol%	Coercive Field, Hc	Remanent Magnetization, Mr (emu/g)	Saturation, Ms (emu/g)
x = 0.1	191.23	0.006	0.034
x = 0.2	998.12	0.100	0.355
x = 0.3	3090.10	0.263	1.229

IV. Conclusion

($Pb_{1-x}La_{x/2}Sm_{x/2}$) ($Ti_{1-x}Fe_x$) O_3 (where x = 0.1, 0.2, 0.3) prepared by solid state reaction route. Phase confirmation is done by X-ray Diffraction, single phase tetragonal structure is obtained for x = 0.1

and 0.2 and pure cubic for x = 0.3 which is also confirmed from FESEM and Raman Spectroscopy. Enhanced room temperature ferromagnetism is obtained as the doping of iron is increased in $PbTiO_3$.

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