

# A comparative study of sol-gel and solid-state prepared $\text{La}^{3+}$ doped multiferroic $\text{BiFeO}_3$

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## ABSTRACT

$\text{La}_x\text{Bi}_{1-x}\text{FeO}_3$  (LBFO) samples were prepared by sol-gel route using citric acid as chelating agent for  $x = 0.0 - 0.4$ . The structure, dielectric and magnetic properties of the LBFO compounds were studied and compared with the corresponding properties of the materials prepared by a conventional solid state reaction. The use of the sol-gel method in preparation lowered the reaction threshold temperature by 200 °C. Effects of the preparation routes and conditions on the phase and microstructures of the materials were investigated in this study using XRD and SEM. The pure BFO without bismuth loss, which cannot be prepared by the solid state reaction, was obtained by the sol-gel method. Sol-gel synthesis could yield a pure phase material at relatively lower temperatures while the solid state method yielded powder with a small amount of the secondary  $\text{Bi}_{25}\text{FeO}_{40}$  phase. Single phase LBFO prepared by sol-gel method (SG) revealed huge value of dielectric constant than same obtained by the solid state reaction method (SS). Maxwell-Wagner type dielectric dispersion is observed in sol-gel method. Dielectric constant and loss tangent are found to be higher for SG as compared to SS. Huge coercivity ( $H_C$ ) of the order of ~ 15 kOe is observed in both SG and SS samples due to the high anisotropy in these samples. The increase in the magnetization is observed due to the destruction of spin cycloid structure. The enhanced properties made LBFO a promising candidate for the applications in novel memory devices and spintronics. Copyright © 2014 VBRI press.

**Keywords:** Multiferroics; ceramics; magnetic oxides; magnetic properties.

## Introduction

Multiferroics, having the coexistence of magnetic and ferroelectric orders, have attracted the attention of many researchers due to its potential applications for magneto-electric devices [1]. Among various types of multiferroic materials, perovskite-type  $\text{BiFeO}_3$  (BFO) is the only room temperature multiferroic till today having the ferroelectric  $T_C = 1043$  K and  $T_N = 647$  K. However, the narrow synthesis area of single-phase BFO would result in the formation of secondary phases such as  $\text{Bi}_2\text{Fe}_4\text{O}_9$  and  $\text{Bi}_{25}\text{FeO}_{40}$  along with BFO. In addition, leakage current and low magnetization in BFO limits its usage in multifunctional devices. The multiferroic properties of BFO are very sensitive to its intrinsic defects, such as vacancies. Highly dense materials without impurities are essential to avoid the leakage current and to exhibit good ferroelectric properties. The densification of these materials very much relies on synthesis route and sintering temperature. Many studies have focused on the synthesis of single phase BFO using different techniques. The  $\text{BiFeO}_3$  ceramics with  $R3c$  phase can be made at different temperatures including liquid phase sintering by a conventional solid-state reaction (SS) [2, 3]. But, this method often leads to the volatilization of bismuth oxide and phase decompositions as SS method

involves extensive heating of oxide mixture at higher temperature for densification. On the other hand, the ceramics prepared using sol-gel technique (SG) shows better reactivity than solid state reaction and fully densified samples can be obtained at a relatively lower temperature (~750°C). The sol gel procedure involves molecular level mixing and results in the homogeneous material [4]. The SG technique also has an advantages over SS like low cost, generates less carbon residue and easy to prepare. Hence sol-gel has been considered as an alternative method for the preparation of BFO. It is also noted that the La doping in BFO is a very effective way to reduce the leakage current and also to release the potential magnetization locked in the spiral spin structure [5, 6].

In this study, the focus is to understand the effect of the synthesis routes on (i) the structural transition with respect to the La content, (ii) the dielectric properties and (iii) magnetic behaviour of these compounds. To achieve above mentioned objectives, we have synthesized  $\text{La}_x\text{Bi}_{1-x}\text{FeO}_3$  ( $x = 0 - 0.4$ ) ceramics using SS and SG methods and refined the structure considering the  $R3c$  and  $P6mm$  structural models for the bulk samples. The observed structural changes and the effect of the synthesis route are correlated with dielectric and magnetic studies on these samples.

## Experimental

### Materials

$\text{La}_x\text{Bi}_{1-x}\text{FeO}_3$  (LBFO) ceramics with  $x = 0, 0.05, 0.1, 0.2,$  and  $0.4$  powders were prepared via solid state and sol-gel methods. High-purity (99.9 %)  $\text{La}_2\text{O}_3$ ,  $\text{Bi}_2\text{O}_3$  and  $\text{Fe}_2\text{O}_3$  of Sigma- Aldrich make were used as the starting materials for the solid-state reaction synthesis. To prepare the LBFO using sol-gel method; the precursors, high purity (99.9 %)  $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ ,  $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$  and  $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$  of Sigma- Aldrich make were used.

### Synthesis of LBFO using solid-state reaction

The  $\text{La}_2\text{O}_3$ ,  $\text{Bi}_2\text{O}_3$  and  $\text{Fe}_2\text{O}_3$  were taken in stoichiometric proportions and thoroughly mixed thoroughly under ethanol medium using a ball mill for 4 h. The ball milling was carried out in a Retsch single station (PM-100) planetary ball milling system in air. A 125 ml tungsten carbide vial and tungsten carbide balls with a diameter of 10 mm, 5 mm and 3 mm were used. The milling speed was set at 350 rpm, and it was stopped for every 30 min of milling for a duration of 2 min to cool down the system, and the balls direction was reversed for further grinding. Then the mixture was pre-calcined at 600 °C for 30 min followed by the calcination at 820 °C for 1 h. Further, pellets were made and sintered at 800 °C for 4 h.

### Synthesis of LBFO using sol-gel method

The precursors in a stoichiometric molar ratio were dissolved in 1:5  $\text{HNO}_3$  to form an aqueous solution. Citric acid was then added in appropriate proportion and stirred for 2 h at RT. Then, the mixture was heated at 250 °C on a hot plate with stirring, which leads to the evolution of gases. The brownish colour residue obtained finally, was heated at 600 °C for 1h to form the desired compound. These powders are made into pellets and sintered for densification at 750 °C for 4 h.

### Characterization

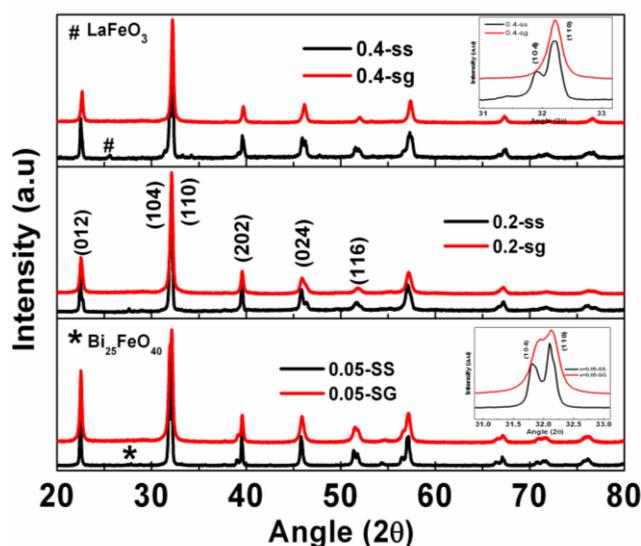
Room temperature X-ray diffractogram was recorded on these ceramics using Bruker D8 X-ray diffractometer with  $\text{Cu K}_\alpha$  wavelength (1.5418 Å). The samples were characterized for its microstructure using Carl Zeiss Ultra 55 Field emission scanning electron microscopy (FE-SEM) and for chemical composition using Energy dispersive X-ray fluorescence (EDS) analysis. For electrical measurements, silver electrodes were formed on both sides of the sample discs to make capacitor geometry. Dielectric constant ( $\epsilon_r$ ) measurements were carried out using Agilent E4980A LCR meter at room temperature (RT). Hysteresis loops were recorded using Quantum Design PPMS-VSM at 300 K by sweeping the external field between  $-7\text{T}$  to  $+7\text{T}$ .

## Results and discussion

### X-ray diffraction

The X-ray diffraction patterns of LBFO prepared using solid state synthesis as well as sol gel route, are shown in **Fig. 1**. XRD data for pure samples shows a minor secondary phase corresponding to  $\text{Bi}_{25}\text{FeO}_{40}$  for SS where

as a clear single phase is found for SG prepared sample. From the figure, the pure BFO is easily indexed as rhombohedral structure with the  $R3c$  symmetry and it matches with the standard data (JCPDS card no. 86-1518). The secondary phase is absent for all the dopant samples for SS and SG as La doping helps in stabilization of  $R3c$  phase of BFO even for  $x = 0.05$ . A small section of XRD pattern in the range of  $31^\circ$ – $33^\circ$  (inset of **Fig. 1**) shows that the intensity of (1 0 4) diffraction peak suppresses while the intensity of (1 1 0) peak rises as  $x$  increases accompanied by a shift towards higher angles seen more prominently in the case of SG sample. These occurrences are due to a gradual structural phase transition from the distorted rhombohedral  $R3c$  to orthorhombic  $Pbnm$ . The larger ionic substitution of  $\text{La}^{3+}$  ( $r = 1.22$  Å) for  $\text{Bi}^{3+}$  ( $r = 1.14$  Å) results in the large crystal distortion and results in the structural transition. The Rietveld refinement carried out on the LBFO reveals it in  $R3c$  phase up to  $x = 0.2$  and the structure changes to  $Pbnm$  for  $x > 0.2$  and these are consistent with earlier reports [7].



**Fig. 1.** XRD pattern of  $\text{La}_x\text{Bi}_{1-x}\text{FeO}_3$  ( $x = 0.05, 0.2$  and  $0.4$ ) samples prepared by solid state and sol-gel methods.

The pure samples fit well for the  $R3c$  symmetry and obtained refinement parameters for the SS and SG samples are  $a=b= 5.62$  Å,  $c= 13.69$  Å and  $a=b= 5.57$  Å,  $c= 13.87$  Å respectively. Whereas for  $x=0.4$ , a better fit is observed with orthorhombic  $Pbnm$  symmetry with the lattice parameters;  $a= 5.49$ ,  $b= 5.53$  Å,  $c= 7.59$  Å and  $a=5.60$  Å,  $b=7.81$  Å,  $c=5.43$  Å for SS and SG samples.

### Morphology

In order to find the grain size distribution in La doped BFO, the morphology of LBFO has been studied using FE-SEM. The density of SG prepared samples is higher as compared to the SS preparation. As shown in the **Fig. 2**, morphological characteristic on these samples exhibited that the sol-gel synthesis resulted in materials with a finer average particle size ( $\sim 0.6$  μm) compared to powder synthesized via the solid state reaction method ( $\sim 0.9$  μm). It is clear that the grain growth found to be suppressed with increase in La content and helps in densification. The

chemical compositions of pure and doped BFO samples were determined using EDS technique. Besides the obvious signals for O, Bi, and Fe elements, the EDS spectra show a weak signal of La in the doped samples. Moreover, the EDS analysis confirms that the chemical composition of LBFO is nearly in stoichiometric ratios.

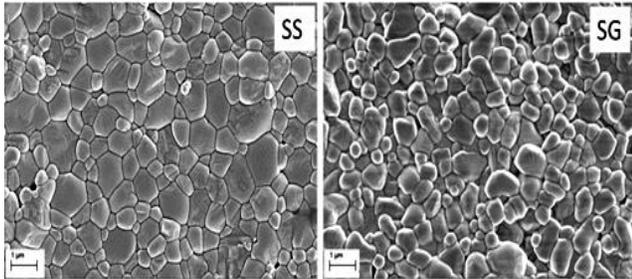


Fig. 2. FE-SEM image of  $\text{La}_x\text{Bi}_{1-x}\text{FeO}_3$  ( $x = 0.05$ ) samples prepared by solid state and sol-gel methods.

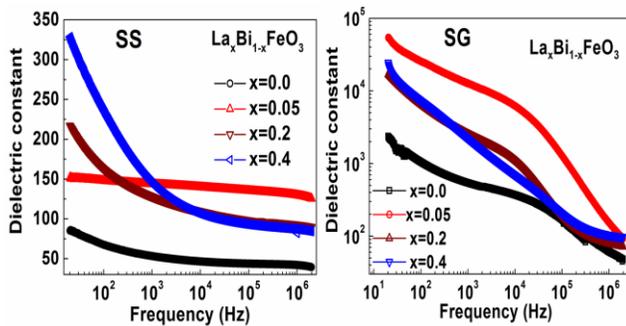


Fig. 3. Dielectric versus frequency graph of  $\text{La}_x\text{Bi}_{1-x}\text{FeO}_3$  ( $x = 0.05, 0.2$  and  $0.4$ ) samples prepared by SS and SG methods.

Table 1. Comparison of Dielectric and Magnetic parameters for  $\text{La}_x\text{Bi}_{1-x}\text{FeO}_3$  ( $x = 0.05, 0.2$  and  $0.4$ ) samples prepared by SS and SG.

La content	Solid state				Sol gel			
	Magnetic parameters			Dielectric constant	Magnetic parameters			Dielectric constant
	300K				300K			
	$H_C$ (kOe)	$M_r$ (emu/g)	$M$ (emu/g)	1kHz	$H_C$ (kOe)	$M_r$ (emu/g)	$M$ (emu/g)	1kHz
$x = 0.0$	0.32	$5 \times 10^{-4}$	0.40	53.23	0.853	$5.4 \times 10^{-4}$	0.40	538.89
$x = 0.05$	12.1	0.13	0.66	127.91	5.91	0.076	0.613	12,696
$x = 0.2$	13.9	0.24	0.83	143.72	10.23	0.259	0.802	2520
$x = 0.4$	14.8	0.21	0.81	145.01	19.46	0.274	0.821	2187

Dielectric properties

The variation of dielectric constant ( $\epsilon'$ ) of these samples as a function of frequency in the range 20Hz- 2MHz prepared by SS as well as SG route is shown in Fig. 3. The dielectric constant of sol gel synthesized samples is very much higher as compared to solid state synthesized samples (Table 1). From the figure, the maximum value of dielectric constant can be observed at  $x = 0.05$  in case of SG whereas a maximum in  $\epsilon'$  is observed for  $x = 0.4$  for SS. It is clearly observed that all the SG prepared samples have a very high value of dielectric constant in low frequency region in

comparison with the previous reports in other RE doped  $\text{BiFeO}_3$  [8, 9]. Similar kind of dielectric behaviour with large value of dielectric constant has been found in citric acid route prepared  $\text{SmFeO}_3$  [10] and also in other materials prepared using hydrothermal synthesis [11]. This kind of behaviour exhibiting high dielectric constant at low frequency and the low value at high frequency is a mark of large Maxwell-Wagner type dielectric dispersion [12]. The space charge polarization in these samples may result into such high value of dielectric constant at low frequencies.

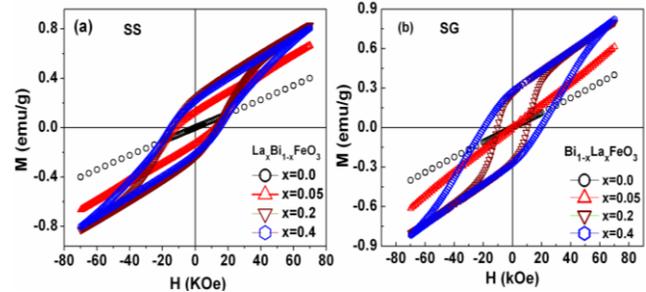


Fig. 4. M-H loops of  $\text{La}_x\text{Bi}_{1-x}\text{FeO}_3$  ( $x = 0.05, 0.2$  and  $0.4$ ) samples prepared by solid state and sol-gel methods at room temperature.

Magnetic properties

The magnetic hysteresis loops of LBFO samples with  $x = 0.0, 0.05, 0.2$  and  $0.4$  are measured by applying a field of 7T at 300K is shown in Fig. 4. The M-H curve of the  $x = 0.0$  sample show a linear field dependence of magnetization ( $M$ ) indicating the antiferromagnetic nature of undoped BFO. The G-type AFM in BFO limits the higher magnetization; however the canting angle between the spins of Fe sub-lattices results in a net residual magnetic moment [13]. The potential magnetization locked in the spin cycloid of the BFO can be released by destroying the cyclic spin structure upon La doping. Remarkable enhancement in the coercivity ( $H_C$ ) and remanence ( $M_r$ ) is observed with La, which is a clear indication of the transition from antiferromagnetic to ferromagnetic behaviour. The systematic increase in  $M_r$  with  $x$  is due to the gradual collapse of the space-modulated spin structure of BFO. The  $M$  measured at 7 T increases linearly with  $x$  and a maximum value is found for SG samples (0.81 emu/g for  $x = 0.4$ ).  $M_r$  for BFO at RT almost vanishes and increases gradually with  $x$  reaching maximum value for  $x = 0.4$  (0.274 emu/g, 0.24 emu/g for SG and SS respectively). This is in good agreement with the change in the crystal structure caused by La doping. For  $x \leq 0.2$  the structure remains in  $R3c$ , whereas a change in the structure to  $Pbnm$  is observed for  $0.2 < x \leq 0.4$ . Thus, both the canting angle of the spins and the cycloid spin structure has been modified due to the doping. As  $x$  increases, the approach to the saturation in M-H loops starts at lower fields.

The maximum  $H_C \sim 19$  kOe is observed for SG samples whereas SS sample shows 14.8 kOe for  $x = 0.4$ . All the measured magnetic parameters are listed in the Table 1. The observed  $H_C$  in both the preparation methods is the highest reported to the best of our knowledge for the RE doped BFO system. The huge coercivity of the order of  $\sim 15$  kOe at RT is also observed in the other non RE dopant systems [14, 15]. The increase in the  $H_C$  is associated to the

doping-driven increase in the magnetic anisotropy [16]. La substitution changes the crystal field of ligands there by induce the anisotropy and the change in anisotropy can also be interpreted due to the change in spontaneous polarization through the chemical pressure [17, 18]. The enhanced magnetic anisotropy mainly comes from magneto crystalline anisotropy and magnetoelastic anisotropy [19]. Further studies are needed to compliment the details of the high magnetic anisotropy in La-doped BFO.

## Conclusion

Lanthanum doped bismuth powders were prepared using solid state as well as sol gel method using citric acid as complexing agent. The  $R3c$  structure changes to orthorhombic  $Pbnm$  phase as the La doping increases. The smaller particle size  $\sim 0.4 \mu\text{m}$  of SG prepared samples results in the high densification and the dielectric constant increases. A large dielectric constant of the order of  $10^5$  is observed for the SG samples which required further understanding. M-H loops show a huge coercivity in both SG and SS samples due to the high anisotropy in LBFO samples. The increase in the magnetization of these samples is due to the destruction of spin cycloid structure.

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