Origin of giant dielectric permittivity and weak ferromagnetic behavior in $(1-x)\text{LaFeO}_3-x\text{BaTiO}_3$ ($0.0 \leq x \leq 0.25$) solid solutions

T. Sreenivasu^{*,§}, P. Tirupathi[†], K. Prabakar[‡], B. Suryanarayana^{*} and K. Chandra Mouli^{*}

^{*}Department of Engineering Physics, Andhra University College of Engineering
Visakhapatnam-530003, India

[†]Department of Physics

Rajiv Gandhi University of Knowledge Technologies (AP-IIIT)
RK Valley-516330, India

[‡]Advanced Magnetic Group

Defense Metallurgical Research Laboratory
Hyderabad-500058, India
[§]seenu.t2007@gmail.com

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The solid solutions of $(1-x)\text{LaFeO}_3-x\text{BaTiO}_3$ ($0.0 \leq x \leq 0.25$) have been synthesized successfully by the conventional solid-state reaction method. Room temperature (RT) X-ray diffraction studies reveal the stabilization of orthorhombic phase with Pbnm space group. Complete solubility in the perovskite series was demonstrated up to $x = 0.25$. The dielectric permittivity shows colossal dielectric constant (CDC) at RT. The doping of BaTiO_3 in LaFeO_3 exhibit pronounced CDC up to a composition $x = 0.15$, further it starts to decrease. The frequency-dependent dielectric loss exhibits polaronic conduction, which can attribute to presence of multiple valence of iron. The relaxation frequency and polaronic conduction mechanism was shifted towards RT as function of x . Moreover, large magnetic moment with weak ferromagnetic behavior is observed in doped LaFeO_3 solid solution, which might be the destruction of spin cycloid structure due to insertion of Ti in Fe–O–Fe network of LaFeO_3 .

Keywords: Multiferroic; ferromagnetic; ceramics.

1. Introduction

Multiferroic ceramics are characterized by simultaneous presence of two or more ferroic order parameters and coupled via magnetoelectric interaction.^{1,2} In last few decades, single-phase multiferroic materials has received considerable attention in novel device applications owing to extra degree of freedom via coupling between the ferroic order parameters.^{1,2} The cross coupling between electric field by magnetization or magnetic field by polarization leads to accomplish large number of magnetic, electric and magnetoelectric properties to meet the desperate urge for miniaturized and integrated devices. Among reported single-phase multiferroics, BiFeO_3 and BiMnO_3 are most prominent room temperature (RT) multiferroics. Recently, LaFeO_3 ceramics also gained considerable attention for high potential applications in thermodynamics, mechanics and sensing applications due to its multiferroic character and colossal dielectric constant (CDC). LaFeO_3 exhibit orthorhombic distorted perovskite unit cell with Pbnm space group. It contains only trivalent iron and exhibiting a high value of the Neel temperature ($T_N \sim 477^\circ\text{C}$) and ferroelectric transition at 830°C .^{3,4}

As a fact most of the transition metal ions have been proved to be one of the most prominent CDC materials. Ever

since, these material suffers multiple valance ($\text{Fe}^{3+}/\text{Fe}^{2+}$, $\text{Ti}^{4+}/\text{Ti}^{3+}$, $\text{Mn}^{3+}/\text{Mn}^{4+}$) which can be correlated with oxygen vacancies is a common feature for the CDC effect in transition metal ions.^{5–11} Worthwhile, LaFeO_3 ceramic also exhibit CDC up to 380 K. For the first time, Idress *et al.*¹² reported a giant dielectric constant behavior in LaFeO_3 , which was an extrinsic effect due to Maxwell–Wagner relaxation.^{11,12} Despite, it has few limitations, such as high leakage current, intrinsic antiferromagnetic and weak ME coupling at RT, which can hamper the large scale applications.

In order to overcome, the intrinsic limitations of LaFeO_3 , various strategies are being investigated to improve the ME performance of LaFeO_3 at RT. Among, the synthesis of solid solution with strong ferroelectric materials i.e., $\text{LaFeO}_3-\text{ATiO}_3$ ($A = \text{Pb}^{2+}, \text{Ba}^{2+}, \text{Sr}^{2+}$) is most acceptable.^{13–15} The doping of BaTiO_3 in LaFeO_3 can influence dielectric permittivity as well as the magnetic properties due to mismatch in ionic radii (Fe/Ti) and multiple valance states of Ba/La ($2+/3+$) or Fe/Ti ($3+/4+$). So far there are no reports which deal with CDC behavior in $\text{LaFeO}_3-\text{BaTiO}_3$ solid solutions. Keeping these in view, we have prepared $(1-x)\text{LaFeO}_3-x\text{BaTiO}_3$ a series of solid solutions. The present work also reports/reexamine the physical properties of parent compound

LaFeO₃ and its solid solution $(1-x)\text{LaFeO}_3-x\text{BaTiO}_3$ ($0.0 \leq x \leq 0.25$). The details of structural and microstructural, low temperature dielectric and magneto-electric properties are presented in the present paper.

2. Experimental Procedure

The ceramic sample $(1-x)\text{LaFeO}_3-x\text{BaTiO}_3$ ($0.0 \leq x \leq 0.25$) was synthesized by conventional solid-state reaction method. The raw material was commercial 99.9% purity La₂O₃, BaCO₃, TiO₂ and Fe₂O₃ were weighed, mixed thoroughly and calcined at 1300°C in air for 12 h. The repeating calcinations and grinding was carried in anticipation of secondary phase. The phase purity of the final powder was analyzed using X-ray diffractometer (PHILIPS-PW3373 XPERT-PRO) with CuK_α radiation ($\lambda = 1.5405\text{\AA}$) in the 2θ range 20–80°. Further, sintering process was carried out at 1350°C in air for 8 h. The surface morphology and microstructural features of sintered pellet were obtained using a field emission scanning electron microscope (FESEM CARL ZEISS SUPRA 40). The dielectric data was collected using LCR meter in the frequency range 100 Hz–1 MHz, while keeping the electrode pellets in sandwich geometry. The magnetic measurements were done with the help of SQUIDE-VSM magnetometer with the field strength of 6 Tesla.

3. Results and Discussion

Figure 1(a) shows the RT X-ray diffraction (XRD) pattern of $(1-x)\text{LaFeO}_3-x\text{BaTiO}_3$ ($0.0 \leq x \leq 0.25$) ceramics. The observed diffraction peaks indicate crystalline in nature, and good homogeneity. The lattice parameter calculation was carried by using orthorhombic crystal system with Pbnm space group. The lattice parameters and crystallite size was given in Table 1, which are obtained by using Scherrer formula. The obtained lattice parameters decrease with substitution of BaTiO₃ in LaFeO₃ are in agreement with insertion of smaller ionic size of the Ti⁴⁺ ion in Fe³⁺ (0.645 Å and

Table 1. Variation of lattice parameters, crystallite size with composition obtained by considering orthorhombic unit cell with Pbnm space group.

Composition (1 - x)	Lattice parameters	Crystallite size (nm)
LaFeO ₃ -xBaTiO ₃		
X = 0.0	a = 5.5507 Å, b = 5.5522 Å, c = 7.8572 Å	195
X = 0.05	a = 5.5494 Å, b = 5.5581 Å, c = 7.8548 Å	193
X = 0.10	a = 5.5491 Å, b = 5.5592 Å, c = 7.8532 Å	191
X = 0.15	a = 5.5485 Å, b = 5.5602 Å, c = 7.8530 Å	168
X = 0.20	a = 5.5482 Å, b = 5.5602 Å, c = 7.8526 Å	174
X = 0.25	a = 5.5481 Å, b = 5.5605 Å, c = 7.8522 Å	171

0.605 Å for Fe³⁺ and Ti⁴⁺, respectively).¹³ The peak profile in the intervals of $31^\circ \leq \theta \leq 34^\circ$ (magnified view) is also shown in Fig. 1(b) in closer inspection. Large deviation in peak position and peak splitting is clearly observed at $x = 0.15$ composition, which indicates structural phase transition near at $x = 0.15$ composition. Moreover, the noted crystallite size also decreases with increasing BaTiO₃ concentration in LaFeO₃ up to $x = 0.15$, after that starts to increase is also shown in Fig. 2. This further becomes evidence for confirmation of phase transition boundary at $x = 0.15$. Since LaFeO₃ is orthorhombic with Pbnm crystal system and BaTiO₃ system is tetragonal with P4mm unit cell, the observed phase transition could be orthorhombic to tetragonal. For detailed structural phase transition analysis Neutron diffraction study with Rietveld refinement method is essential. (The work is under progress.) Furthermore, to understand the dielectric and magnetic properties of LFBT ceramics, the bond length and bond angle calculations are also essential. We calculated bond angle in LFBT systems, the observed bond angle between Fe–O₁–Fe is 154.75° for $x = 0.0$, for $x = 0.10$ is 154.78° and for $x = 0.20$ is 155.25°. The noted bond angle increases with increasing x , which indicate the doping of BaTiO₃ in LaFeO₃ reduce the unit cell volume and straightening Fe–O₁–Fe bond angle.

Fig. 1. XRD pattern of the $(1-x)\text{LaFeO}_3-x\text{BaTiO}_3$ ($0 \leq x \leq 0.25$) solid solution ceramics.

Fig. 2. Variation of crystallite size with compositions for the $(1-x)\text{LaFeO}_3-x\text{BaTiO}_3$ ($0 \leq x \leq 0.25$) solid solution.

Fig. 3. Scanning electron microscope pictures of $(1-x)\text{LaFeO}_3-x\text{BaTiO}_3$ ($0 \leq x \leq 0.25$) ((a) $x = 0.0$, (b) $x = 0.05$, (c) $x = 0.10$, (d) $x = 0.15$, (e) $x = 0.20$, (f) $x = 0.25$) solid solutions.

Figures 3(a)–3(f) show the typical SEM micrographs of LFBT solid solutions. The observed grains are spherical in shape and nonuniform distribution with high dense. The average grain size calculated from the micrograph of $x = 0.0$ is $5\text{--}10\ \mu\text{m}$. While with doping of BaTiO_3 in LaFeO_3 the grain size decreases, the calculated size is $5\text{--}7\ \mu\text{m}$, $3\text{--}5\ \mu\text{m}$ ranges for $x = 0.10$ and $x = 0.15$, respectively. The decrease in grain size with increase of BaTiO_3 concentration up to $x = 0.15$ is observed. Further doping of BaTiO_3 in LaFeO_3 increases the grain size. The decrease in grain size with increase of BaTiO_3

concentration is due to substitution of smaller ionic size element/ion Ti^{4+} ($0.605\text{\AA}$) at the larger ionic size element Fe^{3+} ($0.645\text{\AA}$) ion. Worthwhile these observations are well agreed with lattice parameter calculations.

Figures 4(a)–4(d) show the variation of dielectric constant with temperature in frequency range of $100\text{ Hz--}1\text{ MHz}$ for LFBT ceramics in the intervals of $80\text{--}350\text{ K}$. It can be seen that the sample $x = 0.00$ i.e., LaFeO_3 exhibits similar CDC behavior to that reported in $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$. The noted dielectric constant increase monotonically from 80 K to RT ,

Fig. 4. (a)–(d) Variation of dielectric permittivity with temperature in different frequencies of $(1-x)\text{LaFeO}_3-x\text{BaTiO}_3$ ($0 \leq x \leq 0.25$) ((a) $x = 0.0$, (b) $x = 0.10$, (c) $x = 0.15$, (d) $x = 0.20$) solid solutions.

which behaves as a weak temperature-dependent plateau with a high value (> 2550) at RT, then it decreases stepwise to a flat value of 20 at 80 K. Worthwhile these observation are well agreed with previous reports by Chen *et al.*¹⁶ Further for $x = 0.10$ (shown in Fig. 4(b)) solid solution also exhibit similar behavior which decreases stepwise, where the low temperature dielectric constant is > 40 (at 80 K) and at RT it was > 4000 . The noted values are slightly higher than that of pure LaFeO_3 ceramic. Whereas, for $x = 0.15$ the noted dielectric constant increase rapidly from 200 K to RT, which behaves as a weak temperature-dependent plateau with a high value (> 2230) at RT, then it decreases stepwise and independent of temperature of 200–80 K intervals. Similar observation also can be seen for $x = 0.20$ composition. The rapid rise in dielectric constant was shifted towards to RT for $x = 0.15$ and 0.20, respectively.

Figures 5(a)–5(d) show the variation of dielectric loss with temperature of LFBT ceramics respectively. Irrespective of the composition, the noted dielectric loss peaks are frequency dependent with the increasing frequency, the peak position shifts towards a higher temperature, accompanying a slight increase in the peak intensity. For high composition $x = 0.15$ and $x = 0.20$ the dielectric relaxation peak positions are shifted towards RT. These observations indicate that the noted

dielectric loss relaxation is frequency dependent. In order to understand the quantitative nature of the characteristic relaxation frequency and activation energies of the above solid solutions, we fitted frequency-dependent dielectric loss by using Arrhenius expression, $f = f_0 \exp(-E_a/kT_m)$, where f_0 , E_a , T_m have their usual meaning. We plotted $\ln f$ versus $1/T_m$ shown in Fig. 7. It was well fitted in two different regions one at low temperatures below 200 K, and another one at 200 K above. The extracted activation energies and relaxation time are also slit variation in low temperature region below 200 K denoted as Region-I and to above 200 K Region-II. The noted activation energies and relaxation time are reported in Table 2. The noted activation energies decreases with increasing concentration. Frequency-dependent loss in dielectric relaxation peaks indicates polaronic conduction relaxation mechanism.^{17–19} Polaronic conduction can be explained by considering formation of mixed valence state ($\text{Fe}^{2+}/\text{Fe}^{3+}$) and oxygen vacancies. The origin of $\text{Fe}^{3+}/\text{Fe}^{2+}$ and oxygen vacancies are due to defect formation during high temperature sintering process, which cannot avoid normal conventional synthesis process.¹⁹

It can be explained by considering the polaron hopping relaxation due to formation of mixed valence state ($\text{Fe}^{2+}/\text{Fe}^{3+}$) and oxygen vacancies (V^{O}). This will lead to create

Fig. 5. (a)–(d) Variation of dielectric loss with temperature in different frequencies of $(1-x)\text{LaFeO}_3-x\text{BaTiO}_3$ ($0 \leq x \leq 0.25$) ((a) $x = 0.0$, (b) $x = 0.10$, (c) $x = 0.15$, (d) $x = 0.20$) solid solutions.

leakage current, such leakage current is widely accepted that it originated from the formation of $V^{\bullet\bullet}$ and the valence transformation from Fe^{3+} to Fe^{2+} . The energy levels associated with the unbonded ($V^{\bullet\bullet}$) are very close to the conduction band, so the electrons can be readily activated to be free for conduction by the electric field. When excess charge carriers, such as electrons/holes ($V^{\bullet\bullet}$) are present in a crystal,

the atoms in their environment are polarized and displaced producing a local lattice distortion. In present ceramics also, it is reported that mixed valence states are also possible due to high sintering condition. Hence, in LFBT the Fe^{3+} and Fe^{2+} form a link between $\text{Fe}^{3+}-\text{O}-\text{Fe}^{2+}$ bonds. Under the applied field, the $\text{Fe}-3d$ electrons in Fe^{3+} ions can hop to Fe^{2+} . Thus the formation of Fe^{2+} ions will distort the lattice, and produce a polaronic distortion. The noted activation energies agree well with that of the polaronic relaxation due to electron hopping between Fe^{2+} and Fe^{3+} whose activation energy value was widely reported to be around 0.32 eV for BiFeO_3 ceramics, 0.21 eV for YFeO_3 .^{20–22}

Figures 7(a)–7(f) show magnetic hysteresis loops of $(1-x)\text{LaFeO}_3-(x)\text{BaTiO}_3$ ($x = 0.0, 0.05$) at fixed temperature with maximum field of 6T. Normally, the LaFeO_3 system is either weakly ferromagnetic (WFM) or antiferromagnetic (AFM) with a Neel temperature $T_N \sim 477^\circ\text{C}$.^{4,8,9} The net resultant magnetic moment in LaFeO_3 is due to Fe^{3+} ion only, as the La ions also possess small net magnetic moment due to 4f lone pair electrons,¹³ which is small when compared with Fe ion. Magnetic hysteresis loops of LaFeO_3 measured at different temperatures 5, 50, 150 and 300 are shown in Fig. 7(a). The observed loops are not saturated, even with a field of 6 Tesla. These crystals have net ferromagnetic

Fig. 6. $\ln f$ versus $1/T_m$ fitted curves of $(1-x)\text{LaFeO}_3-x\text{BaTiO}_3$ ($0 \leq x \leq 0.20$) solid solutions.

Fig. 7. M - H loops of $(1-x)\text{LaFeO}_3-x\text{BaTiO}_3$ ($0 \leq x \leq 0.25$) ((a) $x = 0.0$, (b) $x = 0.05$, (c) $x = 0.10$, (d) $x = 0.15$, (e) $x = 0.20$, (f) $x = 0.25$) solid solutions at different temperatures.

Table 2. Calculated activation energies and relaxation frequencies.

Sample	Activation energies (E_a)		Free exponential relaxation time (τ_0)	
	Region-I	Region-II	Region-I	Region-II
$x = 0.00$	60.5 m eV	59.2 m eV	7.55×10^{-6} s	6.75×10^{-6} s
$x = 0.10$	56.5 m eV	57.1 m eV	9.22×10^{-6} s	10.2×10^{-6} s
$x = 0.15$	51.5 m eV	50.8 m eV	8.45×10^{-6} s	8.5×10^{-6} s
$x = 0.20$	48.2 m eV	49.1 m eV	9.34×10^{-6} s	10.1×10^{-6} s

moments due to Fe^{3+} , and the remnant magnetizations are approximately 0.085–0.10 emu/g which is independent of temperatures, this suggest that Fe^{3+} spins are not perfectly antiparallel but slightly canted.^{23,24} In addition, linear dependence of coercivity with temperature (shown in Fig. 7(a)) and large coercivity is up to 1300 Oe at RT, suggesting applications as magnetic storage materials in the future.

Further, $x = 0.05$ to 0.25 compositions are also investigated, as seen in Figs. 7(b)–7(f). With small amount of

Table 3. Variation of saturation and remnant magnetization as well as coercive field of LFBT solid solutions respectively at 5 and 300 K temperatures.

Composition (1 - x)LaFeO ₃ -xBaTiO ₃	Temperature at 5 K	Temperature at 300 K
X = 0.00	$M_s = 1.8270$ $M_r = 0.7745$ $H_c = 16572$	$M_s = 1.8699$ $M_r = 0.6655$ $H_c = 13074$
X = 0.05	$M_s = 8.8601$ $M_r = 3.5516$ $H_c = 2647$	$M_s = 7.6229$ $M_r = 3.3907$ $H_c = 3559$
X = 0.10	$M_s = 9.9726$ $M_r = 3.3424$ $H_c = 1625$	$M_s = 2.6699$ $M_r = 1.1795$ $H_c = 3604$
X = 0.15	$M_s = 3.5184$ $M_r = 1.3900$ $H_c = 2650$	$M_s = 2.699$ $M_r = 1.1905$ $H_c = 3594.87$
X = 0.20	$M_s = 6.9934$ $M_r = 2.4140$ $H_c = 1694$	$M_s = 5.1945$ $M_r = 3.1342$ $H_c = 2363$
X = 0.25	$M_s = 4.1856$ $M_r = 1.6194$ $H_c = 2869$	$M_s = 2.9628$ $M_r = 1.1936$ $H_c = 3703.9$

(a)

(b)

Fig. 8. (a) and (b) Variation of saturation magnetization and coercive field with concentration respectively.

BaTiO₃ substitution at $x = 0.05$, significant change in shape of the $M-H$ loops is noted. The observed loops indicate weak ferromagnetic nature. Further addition of BaTiO₃ in LaFeO₃ results in drastic change in shape of hysteresis loops, saturated magnetization and coercivity values. Details of the noted saturation magnetization, remnant magnetization and coercive field (H_c) are shown in Table 3. The enhancement in magnetic moment (M_r) indicates that the latent magnetization, which was locked in LaFeO₃ within the canted spin structure, is released in solid solution. It is believed that the suppression of the canted spin structure will lead to the appearance of weak ferromagnetic moment in BaTiO₃ doped LaFeO₃ systems. The nonlinear behavior in saturation magnetization and coercive field (H_c) values as function of temperatures is plotted in Figs. 8(a) and 8(b), respectively. The observed saturation values increase with increasing composition up to $x = 0.15$, further increase in composition leads to a sudden fall in M_s value which indicates a distortion in magnetic unit cell. It also clearly indicates phase transition region, which supports our XRD analysis. The enhanced dielectric permittivity and large ferromagnetic character of LaFeO₃-BaTiO₃ solid solutions can be useful for future multifunctional and spintronic devices applications.

In summary, solid solutions of $(1-x)\text{LaFeO}_3-x\text{BaTiO}_3$ ($0.00 \leq x \leq 0.25$) polycrystalline sample were synthesized by conventional solid-state route. The RT X-ray diffraction data show a stabilization of orthorhombic (Pbnm) symmetry. It is also shown that CDC values increase in doped LaFeO₃-BaTiO₃ up to $x = 0.15$. It has been found that frequency-dependent dielectric loss exhibits polaronic conduction, which may be due to the presence of multiple valency of $\text{Fe}^{3+}/\text{Fe}^{2+}$. Remnant magnetization found to increase with doping of BaTiO₃ is attributed to destruction of spin cycloid structure due to insertion of Ti in Fe-O-Fe network of LaFeO₃ lattice. Hence, we can conclude that the doping of BaTiO₃ in LaFeO₃ can enhance ferromagnetic character and giant dielectric constant property, which leads to be useful for future magnetoelectric device applications.

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