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Effect of La and Pb substitution on structural and electrical properties of parent and La/Pb co doped $BiFeO_3$ multiferroic

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ABSTRACT

La/Pb co-doped $BiFeO_3$ compounds were prepared by a solid-state reaction. X-ray diffraction of $BiFeO_3$ (BFO), $Bi_{0.725}La_{0.1}Pb_{0.175}FeO_3$ [BLPFO] showed single phase in nature. BFO crystallize in the rhombohedral distorted perovskite structure (space group-*R3c*) while to that BLPFO crystallize in distorted pseudocubic (*Pm*-3*m*) symmetry which has been confirmed by the Rietveld refinement of the room temperature X-ray powder diffraction data. The effect of La/Pb substitution on dielectric constant, and loss tangent, of the samples was studied at room temperature in a wide range of frequency 10 Hz – 1 MHz. The room temperature dielectric constant of BFO (BLPFO) was ≈ 120 (200). Ferroelectric measurement reveals remnants polarization of BLPFO is about 0.24 $\mu C/cm^2$ at an applied field of 15 kV/cm. Weak ferroelectric effect is observed for co-doped $BiFeO_3$ compound. Copyright © 2014 VBRI press.

Keywords: Multiferroics; X-ray diffraction; dielectric properties; ferroelectric loop.

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Introduction

Multiferroic materials have become an object of interest due to coexistence of two or more of the possible ferroic orders occur simultaneously in single-phase material **[1]**. The multiferroism is indeed a subject of intense research because of their wide range of potential applications, including information-storage device, spintronics, magnetoelectric sensor devices and multiple-state memories. Among various multiferroic materials investigated so far, $BiFeO_3$ is widely studied due to coupling between ferroelectric and magnetic order at room temperature and causing the possibility of room temperature multiferroic devices. In $BiFeO_3$, $6s^2$ lone pair of Bi^{3+} ion introduces an off-center distortion results in a spontaneous polarization, whereas the super exchange interactions between Fe^{3+} ions determine magnetic ordering in this material **[2]**. The single phase $BiFeO_3$ exhibits a rhombohedrally distorted perovskite structure (space group *R*3*c*) with high Curie temperature (T_C ~ 1103 K) and antiferromagnetic Neel temperature (T_N ~ 643 K) **[3, 4]**.

It has been earlier observed that partial substitution of rare-earth (*RE*) or alkaline earth metal ions (Sr) at Bi-site of $BiFeO_3$ **[5-7]** helps in eliminating the secondary phase along with a structural phase transformation and improving the ferroelectric and ferromagnetic properties. A structure phase transition from rhombohedral to orthorhombic is observed in $Bi_{1-x}La_xFeO_3$ near $x = 0.30$ and enhances the magnetoelectric interaction **[5]**. For Nd doped $BiFeO_3$ a rhombohedral structure at $x = 0$, a triclinic structure between $x = 0.05–0.15$, and a pseudotetragonal structure between $x = 0.175–0.2$ is observed **[6]**. Furthermore, the replacement of Bi^{3+} by Sr^{2+} leads to a change of the lattice symmetry from the rhombohedrally distorted perovskite of $BiFeO_3$ to the cubic of $SrFeO_{2.97}$ and results in oxygen deficiency in the lattice **[7]**. The $Bi_{0.9-x}La_{0.1}Nd_xFeO_3$ ($x = 0.05–0.1$) ceramics showed an induced phase transition from rhombohedral to triclinic and monoclinic on subsequent Nd and La doping **[8]**.

For $Bi_{1-x}Pb_xFeO_3$, $0 \leq x \leq 0.30$ prepared by solid-state reaction route, phase transition from pseudotetragonal to pseudocubic symmetry is observed **[9]**. The pseudotetragonal symmetry for $x = 0$ and pseudocubic symmetry for $x = 0.2$ agree well with earlier reported data. However, $Bi_{0.8}La_{0.2-x}Pb_xFeO_3$, showed gradually change in crystal structure from pseudotetragonal to pseudocubic symmetry with Pb substitution increases from $x = 0.0$ to 0.2 as prepared by sol-gel process **[10]**. Looking to the technological importance and quest for revealing the substitutional effect at *A*(Bi)-site, we prepared $BiFeO_3$ [BFO] and $Bi_{0.725}La_{0.1}Pb_{0.175}FeO_3$ [BLPFO] {co-doping of La/Pb} in $BiFeO_3$ by solid state reaction route, and report the structural, dielectric and ferroelectric properties.

Experimental

Materials

The high purity (99.5%, Loba) bismuth oxide (Bi_2O_3), iron oxide (Fe_2O_3), lead oxide (PbO) and lanthanum oxide (La_2O_3) were mixed (stoichiometry) in an agate mortar and pestle to prepare $BiFeO_3$ [BFO] and $Bi_{1-x-y}Pb_yLa_xFeO_3$ ($x = 0.1$; $y = 0.175$) [BLPFO] ceramics. All the chemicals were GR grade and used without any further purification.

Synthesis method

The polycrystalline samples with the formulation of $BiFeO_3$ and $Bi_{0.725}La_{0.1}Pb_{0.175}FeO_3$ were prepared by solid-state reaction route. The dried Bi_2O_3, Fe_2O_3, PbO and La_2O_3 reagents in the desired stoichiometric ratios were wet mixed together. The homogeneous mixed powders were calcined at different temperatures for different duration. BFO powder was calcined in two different steps; (1) 650 ^{o}C for one hour and (2) 830 ^{o}C for one and half hours with intermediate grinding in between to achieve the desired phase **[11]**. The fine calcined powders were mechanically pressed (8 - 10 tones) to make circular pellets of 15 mm diameter and 2 mm thickness. All the pellets were sintering as performed in Bi_2O_3 atmosphere at 850 ^{o}C for six hours for densification.

Characterizations

X-ray diffraction: In order to study phase formation and to carry out preliminary structural analysis of BFO and BLPFO, X–ray diffraction (XRD) were taken using Cu$K_{\alpha1}$ radiation ($\lambda = 1.5406$ Å) of a Bruker D8 Advance X-ray powder diffractometer. The data was collected over the angular range 2θ ($10° < 2\theta < 70°$) with a scanning rate of 2° per minute with a step size of 0.02° at room temperature.

Dielectric measurements

The dielectric constant (ε′) and loss tangent (tanδ) were measured using Novocontrol alpha-ANB impedance analyzer in a wide range of frequencies (10 Hz - 1 MHz) at room temperature. For dielectric measurements, sintered pellets were polished with zero grain emery paper, and coated with high purity silver paste on adjacent faces as electrodes and then dried for 2 hrs at 150 ˚C to make the parallel plate capacitor geometry.

Ferroelectric- polarizations measurement

Ferroelectric-polarizations were measured on silver pasted sintered pellets of BFO and BLPFO ceramics using a ferroelectric loop tracer (Sawyer-Tower circuit).

Results and discussion

Fig. 1 shows the XRD pattern for undoped and La/Pb co-doped $Bi_{0.725}La_{0.1}Pb_{0.175}FeO_3$ ceramics. All the diffraction peaks of parent BFO were indexed in the rhombohedral crystal system (space group *R*3*c*) with a very small amount of non-perovskite $Bi_2Fe_4O_9$ impurity phase (marked by * in **Fig. 1**) [JCPDS Card No. 74-1098]. The reflections of the XRD pattern obtained for the $Bi_{0.725}Pb_{0.175}La_{0.1}FeO_3$ ceramics were indexed in the pseudocubic (*Pm*-3*m*) symmetry. From the inset of the **Fig. 1**, the XRD data showed that the doubly splitted (110) and (104) peaks converted into a single (110) peak. Comparison of XRD of BFO and BLPFO indicate a structural transformation with a continual change of structural parameters in the samples with very small rhombohedral distortion that is to say, the solid solution of the La/Pb doped BFO changes the crystal symmetry from rhombohedral to pseudocubic symmetry.

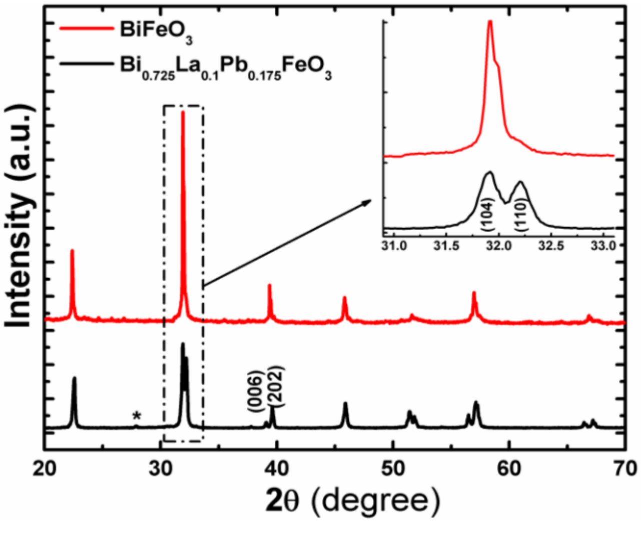

Fig. 1. X-ray diffraction pattern for $BiFeO_3$ [BFO] and $Bi_{0.725}La_{0.1}Pb_{0.175}FeO_3$ [BLPFO] ceramics.

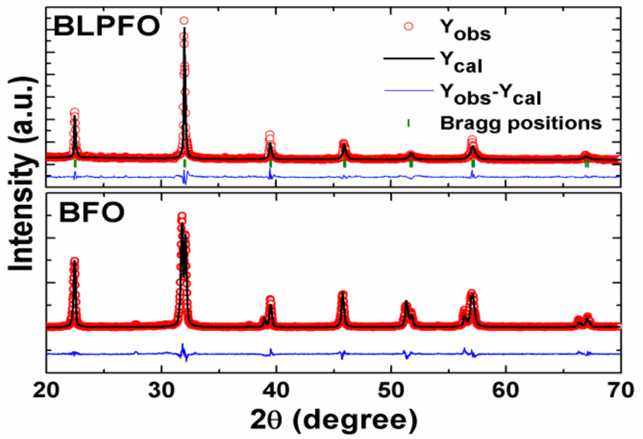

Fig. 2. Rietveld refinement XRD pattern for $BiFeO_3$ and $Bi_{0.725}La_{0.1}Pb_{0.175}FeO_3$ ceramics.

In order to further confirm the structural transition the diffraction pattern were Rietveld refined through Fullprof 2000 program **[12]**. The profile fits for the Rietveld refinement of BFO and BLPFO samples are illustrated in **Fig. 2**. The XRD pattern of parent BFO were refined with rhombohedral (*R*3*c* space group) structure with lattice parameters $a = b \sim 5.5798$ Å and $c \sim 13.867$ Å. whereas, the refined XRD pattern of BLPFO samples was carried out with pseudocubic (*Pm*-3*m*; $a = 3.9491$ Å) symmetry. The obtained lattice parameter matches well with the earlier reported data **[10]**. The calculated parameters of parent as well as doped sample after refinement are listed in **Table 1**. It is noticed that the observed and calculated pattern are in good agreement. The crystal symmetry of both compounds developed by FpStudio Ver-2.0 program is shown in **Fig. 3**.

Table 1. Rietveld refined structural parameters for $BiFeO_3$ and $Bi_{0.725}La_{0.1}Pb_{0.175}FeO_3$ ceramics.

Structure	Cell parameters	Atoms	x	y	z	R-factors (%)
$BiFeO_3$						
*R*3*c*	a = 5.5798 Å	Bi	0.0000	0.0000	0.0000	R_p = 10.2
	b = 5.5798 Å	Fe	0.0000	0.0000	0.2163	R_{wp} = 14.6
	c = 13.860 Å	O	0.5638	0.0197	0.9475	R_{exp} = 7.51
	V = 373.81 $Å^3$					χ^2 = 3.76
$Bi_{0.725}La_{0.1}Pb_{0.175}FeO_3$						
Pm-3m	a = 3.9491 Å	Bi/La/Pb	0.0000	0.0000	0.0000	R_p = 7.05
	b = 3.9491 Å	Fe	0.5000	0.5000	0.5000	R_{wp} = 9.15
	c = 3.9491 Å	O	0.0000	0.5000	0.5000	R_{exp} = 3.95
	V = 61.59 $Å^3$					χ^2 = 4.77

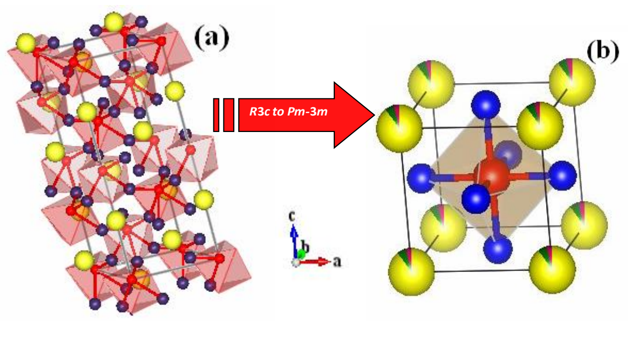

Fig. 3. Representation shows the room temperature rhombohedral (*R*3*c*) structure for $BiFeO_3$ (a) and pseudocubic (*Pm*-3*m*) for La/Pb doped $BiFeO_3$ (b).

Fig. 4 shows the frequency dependent dielectric constant (ε′) and loss tangent (tanδ) of BFO and BLPFO ceramics at room temperature. For higher frequencies, both ε′ and tanδ are independent of frequencies. However, both ceramics exhibited frequency dispersion at lower frequencies. The room temperature values of ε′ at 100 kHz are about 71 and 134 for BFO and BLPFO, respectively. The value of dielectric constant, in this particular frequency range, of BFO and BLPFO is comparable or better than some of the $BiFeO_3$ based systems **[14-16]**. We comment that the room temperature dielectric frequency response infers dispersive characteristics at low frequencies in both BFO and BLPFO, attributed to the presence of oxygen vacancies as well as presence of Fe^{3+} and Fe^{2+} ions on octahedral sites. Usually, the dispersive dielectric permittivity and dielectric loss are concerned with *ac* conductivity. The presence of Fe^{3+} and Fe^{2+} ions on octahedral sites favors the conduction *via* the hopping of charge carriers. The dispersive low frequency dielectric response infers an enhancement of hopping of carriers resulting an increase in the conduction process thereby reducing the resistivity consistent with known dielectric relaxation in solids **[13]**. BLPFO as compare to BFO ceramics discern more dispersion in dielectric constant as well as loss tangent along with their higher values of dielectric constant leading to space charge polarization in multiferroic materials.

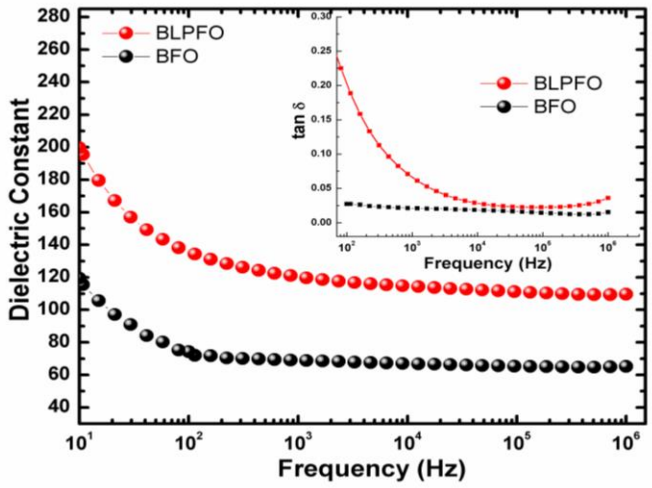

Fig. 4. Variation of ε' and tanδ of the $BiFeO_3$ and $Bi_{0.725}La_{0.1}Pb_{0.175}FeO_3$ as a function of frequency.

The ferroelectric hysteresis loops of BFO and BLPFO at room temperature are shown in **Fig. 5**. Here, it should be mentioned that these values are obtained with different electric fields of 200 [BFO], and 15 [BLPFO] kV/cm, respectively. For the BLPFO, the low resistivity (high dielectric constant and high dielectric loss tangent) makes the ferroelectric measurement difficult.

For parent BFO, the spontaneous polarization mainly comes from the hybridization between $6s^2$ lone electron pair and the 6*p* empty orbital of Bi^{3+} ions, which induce the non-centrosymmetric distortion of the electron cloud and result in the ferroelectricity **[17]**. Under a maximum applied field 160 kV/cm, the remnant polarization ($2P_r$) of the BFO was found to be 18.4 μC/cm^2. Actually for BLPFO, if measured with comparable electric field of BFO, the 2P$_r$ value will be very small, inferring a structural phase transition from rhombohedral to pseudocubic symmetry. We note that BLPFO documents the maximum value of remnant polarization ≈ 0.24 μC/cm^2 at electric field value of 15 kV/cm. We thus comment that 10% La and 17.5% Pb substitution in BiFeO$_3$ retains the ferroelectric phase at room temperature consistent with earlier report **[10]**.

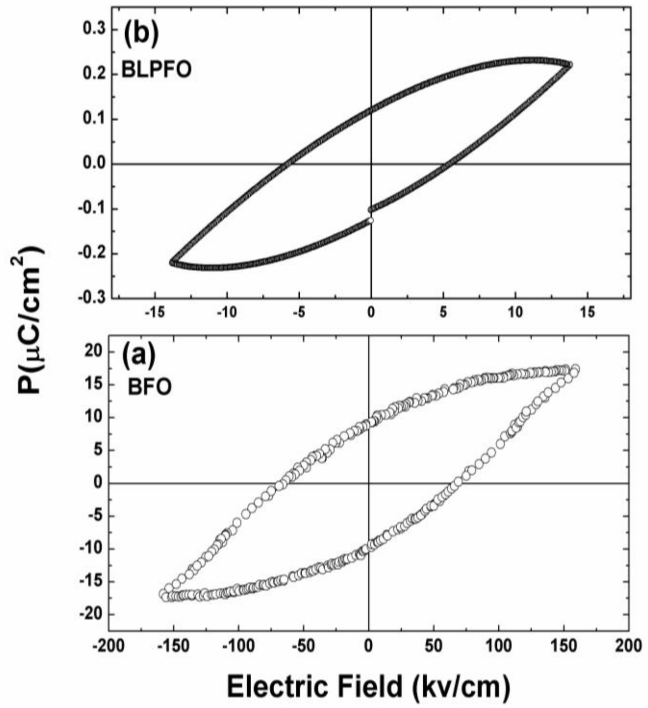

Fig. 5. Room temperature ferroelectric hysteresis loops for BiFeO$_3$ (a) and Bi$_{0.725}$La$_{0.1}$Pb$_{0.175}$FeO$_3$ (b).

Conclusion

In summary, we have investigated the structural and ferroelectric properties of BiFeO$_3$ [BFO] and co-doped Bi$_{1-x-y}$Pb$_y$La$_x$FeO$_3$ (x = 0.1; y = 0.175) [BLPFO] polycrystalline ceramic samples. Rietveld refined X-ray diffraction pattern confirms the formation of single phase and reveal the rhombohedral (space group *R*3*c*) structure for BFO and pseudocubic symmetry (*Pm*-3*m*) for BLPFO compounds. A structural phase transition from rhombohedral [BFO] to pseudocubic symmetry [BLPFO] is obtained. The room temperature dielectric measurements reveal that for higher frequencies, both ε′ and tanδ is independent of frequencies as well both ceramics exhibited frequency dispersion at lower frequencies. The room temperature values of ε′ at 100 KHz are about 71 for BFO and 134 for BLPFO, respectively. The dispersive low frequency dielectric response infers an enhancement of hopping of carriers resulting an increase in the conduction process. Ferroelectric polarization hysteresis loop reveals smaller 2P$_r$ value of BLPFFO as compared to BFO indicating a structural phase transition from rhombohedral to pseudocubic symmetry. With co-doping of La and Pb at Bi site, the ferroelectricity is suppressed as compared to BFO.

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