Structural, Electrical and Magnetic Investigations of Pb-doped $La_{0.1}Bi_{0.90}FeO_3$ Multiferroics

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ABSTRACT

A Sol-gel auto-combustion technique has been employed to synthesize polycrystalline $Bi_xPb_{1-x}FeO_3$ (x =0.0, 0.05, 0.10, 0.20, 0.30) ceramics. The samples have been investigated by X-ray diffraction (XRD), scanning electron microscopy (SEM), vibrating sample magnetometer (VSM) and LCR-meter for its structural, morphological, magnetic and electrical properties, respectively. XRD analysis reveals that Pb doped $La_{0.1}Bi_{0.9}FeO_3$ retains rhombohedral distorted perovskite structure described by the non centro-symmetric space group R3c. The surface morphological studies show that the grain size increases and form agglomerates at high concentrations of Pb. The magnetic properties changes non-monotonically with increasing x. This non-monotonical behavior with increasing x can be attributed to the canting of the antiferromagnetic spins in LBPFO. More interestingly, the dielectric constant of LBPFO has higher values at low frequencies and decreases abruptly with increasing frequencies and becomes almost constant at higher frequencies while it increases slightly with rise in temperature.

1. INTRODUCTION

Multiferroics are the multi-functional materials that exhibit more than one ferroics properties (ferro-electricity, ferro-magnetism and ferro-elasticity) in the same phase (Kreisel 2009). Currently, the research community uses the term 'multiferroics' only for the materials that exhibit both ferro-electricity and magnetism (not necessarily ferro-magnetism) (Khomskii 2006, 2009, Cheong 2007) owing to their potential device applications and fascinating fundamental physics. Low temperature magnetic ordering and weak coupling between magnetism and polarization are, hitherto, a hindrance in the application of these novel materials in devices (Khomchenko 2008). Bismuth ferrite ($BiFeO_3$) is the only material that has ferroelectricity (1103K) and antiferromagnetism (643K) above room temperature and due to this reason, $BiFeO_3$ (BFO) is the most studied material. However, low resistivity, weak ferromagnetism in bulk BFO and its long range cycloildal spin structure have been obstacles in potential device applications (Ramesh 2007). The valance fluctuations on Fe ions and the existence of second

phases are the causes of low resistivity and they can be suppressed by optimizing the fabrication process. Being G-type antiferromagnet (Kadomtseva 2004), overall net magnetization in BFO is zero. The suppression of spin configuration is a necessary condition for the spontaneous magnetization and the linear magnetic effect in BFO and can occur through Dzyaloshinskii-Moriya interaction (Sergienko 2006). This suppression can be achieved by applying large magnetic or electric fields (Ruette 2004), producing epitaxial strains in thin films (Bai 2005) and by doping BFO with suitable ions of transition elements.

The substitution of Fe^{3+} by other transition metal ions (the B-site doping of BFO) has revealed the spontaneous magnetization but this doping decrease the magnetic transition temperature drastically (Azuma 2005). An enhancement of net magnetization has also been reported by A-site substitution with the rare earth magnetic ions like Tb^{3+} (Palkar 2004), Nd^{3+} (Yuan 2006), Sm^{3+} (Yuan 2006), Pr^{3+} (Uniyal 2009). The research on A-site doping with diamagnetic $Bi_{1-x}A_xFeO_3$ (where A = La, Ba, Pb, Sr, Ca) ions has proved to be important for the investigation of the influence of crystal chemistry for weak ferromagnetic movement values and thus contributing to the development of the relationship between the processing crystal structure, magnetic properties and magnetoelectric coupling in BFO based compounds (Khomchenko 2007, 2008, 2009, Troyanchunk 2010, Mazumder 2009). Khomchenko (2008) doped the diamagnetic (Ca, Sr, Pb, Ba) ions and found that the value of the net magnetization strongly depended on the kind of diamagnetic element. The magnetization increases with the increased in ionic radii of the dopant element and the maximum value was achieved for the Ba^{3+}(1.2 emu/g) which had the biggest ionic radii among the other elements. Some groups (Zhang 2009, Ge 2012, Ederer 2005) have concentrated on the Pb doping in BFO because of Pb^{3+} ionic radius is larger than Bi^{3+} and can give enhanced magnetization.

As ionic radius of Pb(133 pm) is greater than Bi (117 pm) and its doping in BFO can enhance the net magnetization, so several groups have concentrated on Pb doping in BFO. Khomchenka (2008) synthesized $Bi_{0.80}Pb_{0.2}FeO_3$ sample by a rapid two stage solid state reaction and carried out its magnetic, dielectric and ferroelectric measurements along with Mossbauer spectroscopy. They got a net magnetization at room temperature. Mazumder (2009) studied dielectric and ferroelectric properties of lightly Pb doped BFO and were able to get improved dielectric properties. Zhang *et al* (2009) used the solid state solution reaction route to get Pb doped $Bi_{1-x}Pb_xFeO_3$ (x = 0.0, 0.1, 0.2, 0.3) and observed the ferroelectricity and magnetism at room temperature. Recently, Ge (Ge 2012) have worked on Pb doping along with La doping $Bi_{1-x}La_{0.2}Pb_xFeO_3$ (x = 0- 0.2) ceramics. The studies showed that the magnetic properties vary non-monotonically whereas ferroelectric properties changed monotonically with increasing x.

In this study, we have carried out the structural, magnetic and dielectric properties of Pb doped $La_{0.1}Bi_{1-x}Pb_xFeO_3$ (x = 0.0, 0.05, 0.1, 0.2, 0.3) ceramics and reported that magnetic and dielectric properties have been improved with increasing x.

2. EXPERIMENTAL PROCEDURES

Polycrystalline samples of pure and Pb doped bismuth ferrite $Bi_xPb_{1-x}FeO_3$ (x =0.0, 0.05, 0.10, 0.20, 0.30) were prepared by using sol-gel auto-combustion technique. The starting materials: $Bi(NO_3)_3.5H_2O$, $Fe(NO_3)_3.9H_2O$, Glycine (as a fuel) $Pb(NO_3)_3$ and $La(NO_3)_3$ were mixed in 100 ml of water in calculated quantity and a few drops of concentrated nitric acid were added to dissolve the bismuth nitrate. Lanthanum nitrate was added to stabilize the phase of bismuth ferrite. The solution was stirred and heated at 90°C for three hours to get a gel. After gel formation, the temperature of the hotplate was raised up to 300°C for complete combustion of the gel. After powder formation, the samples were calcinated at 600°C in a muffle furnace for four hours for annealing purpose. Pallets (D = 16 mm) were made by using a uniaxial pressing at a pressure of 50 Pa and sintered at 600°C for two hours.

The X-ray diffractometer (Rigaku D-max/IIA) with CuK_α radiations (1.5405Å) was used to record XRD patterns of powder samples that was meant to verify the formation of desired material. Furthermore, SEM (Hitachi S3400N) was used for morphological analysis of samples in pallet form. Vibrating sample magnetometer (Lakeshore 7407) was used to investigate the magnetic properties of the samples. Frequency dependent (100Hz-1MHz) dielectric measurements were performed by using LCR meter (Quad Tech 1920).

3. RESULTS AND DISCUSSION

The crystal structure of the samples was determined by XRD. The diffraction patterns of all the samples are given Fig. 1. All the major peaks in the pattern were indexed according to the JCPD card no. 01-071-2494, depicting the prepared samples to contain BFO having rhombohedral structure with the space group R3c. There are no impurities peaks except minor peak of some secondary phase is observed at about $2\theta \approx 34°$ and no effect of Pb doping on this peak has been observed.

In R3c space group, the cations are displaced from their centrosymmetric positions along the threefold symmetric hexagonal [001] axes and produce polarization. Here in case of BFO, polarization is achieved by the antiphase tilt of adjacent FeO_6 octahedra and the displacements of Fe^{3+} and Bi^{3+} cations along [111] directions, from their centro-symmetric positions (Khomchenko 2007). As can be seen in the patterns, the intensity of the diffraction peaks decreases with the increase in Pb doping. Since the peak intensity is related to the amplitude of rotation of the octahedra (Zhang 2009), so the amplitude of tilt of rhombohedral distortion reduces and hence we can say that polarization reduces with increasing lead doping.
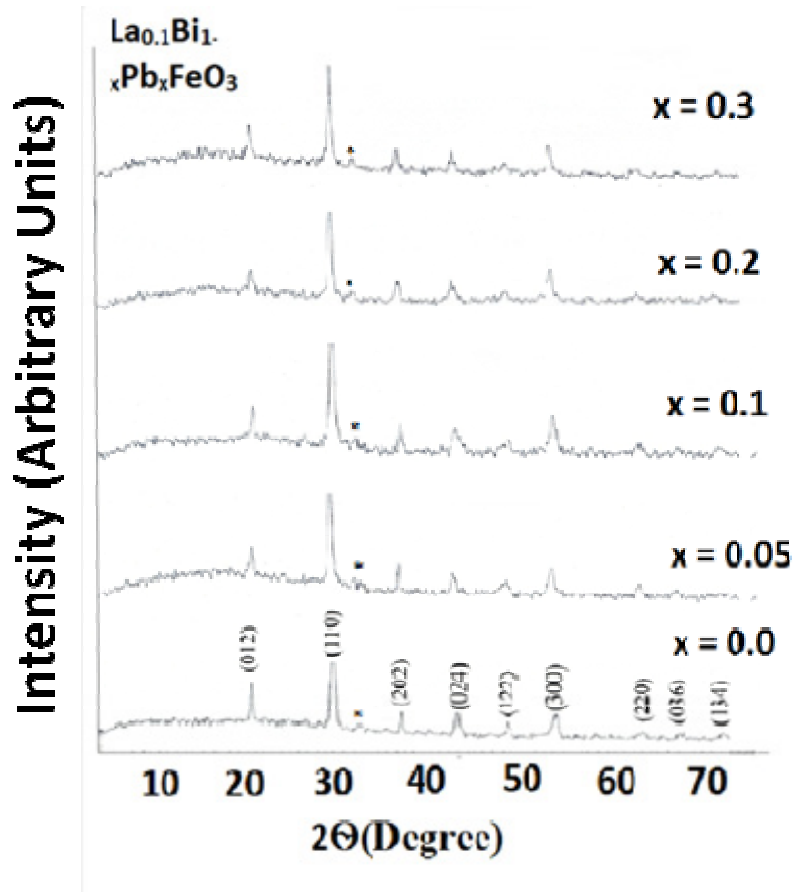
Fig. 1   XRD patterns of all the samples of $La_{0.1}Bi_{1-x}Pb_xFeO_3$ (x = 0.0, 0.05, 0.10, 0.20, 0.30)

The crystallite size of the samples has been calculated from the broadening of X-ray peaks by using the Scherrer formula and the crystallite size increases slightly. The increasing trend in crystallite size with Pb doping can be attributed to the larger ionic radius of Pb^{2+} (133 pm) than Bi^{3+} (117 pm).

A more deep observation of XRD patterns reveals that the reflection peaks shift towards the larger 2θ values as the Pb doping increases. This shift of peaks towards larger angles can be attributed to the contraction of lattice parameters and hence unit cell volume (Uniyal 2009). To confirm this concept, we have calculated the lattice parameters and unit cell volume of all the samples. We observe a decrease in lattice parameter and unit cell volume with the increasing Pb doping. The possible reason for the shifting of peaks towards larger angle and unit cell volume contraction is that the substitution of heterovalent Pb^{2+} on Bi^{3+} requires the appearance of oxygen vacancies or/and Fe^{4+} ions in the lattice due to which unit cell volume reduces (Khomchenko 2008).

The frequency dependent dielectric measurements were taken in the frequency range of 100 Hz to 1 MHz at room temperature. From the graph shown in Fig. 2, it can be seen that the dielectric constant of all the samples have large values at low frequencies (100 Hz) but abruptly decreases as the frequency increases. After a specific frequency value, the dielectric factors do not change and remain almost constant (1 MHz). This dielectric anomaly with frequency can be considered to be due to the combine response of dielectric relaxation which involves the oriental polarization and conduction of charge carriers (Reetu 2011) and can be explained by Maxwell-Wagner model.
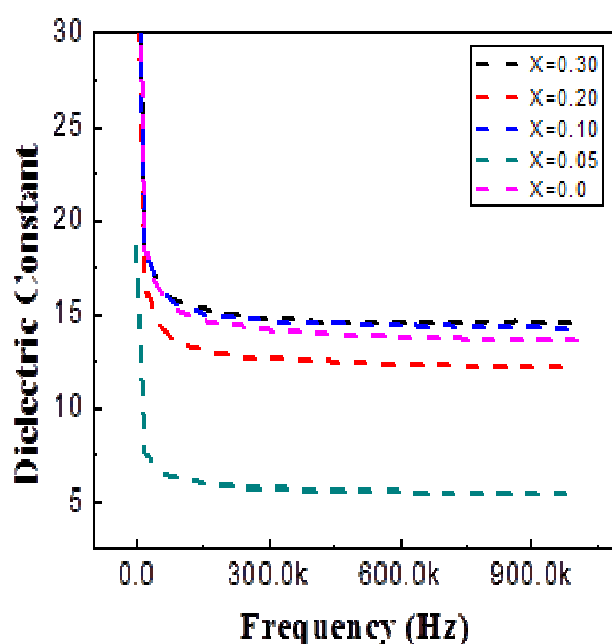

Fig. 2 Dielectric constant plotted as a function of versus frequency for all the samples

At low frequencies, the rotator motion of all the polar molecules of the dielectric material is rapid enough to follow the applied field and hence gives large dielectric constant values. On the other hand at higher frequencies, they lag behind the alternating fields and give low dielectric constant values. The dielectric tangent loss also follows the same trend as dielectric constant, as shown in Fig. 3. Similar trend of dielectric properties has also been reported in Mn (Sahu 2007), Sr (Bhushan 2010), Sm (Yuan 2006), Pr (Uniyal 2009), and Dy (Li 2011) doped BFO.
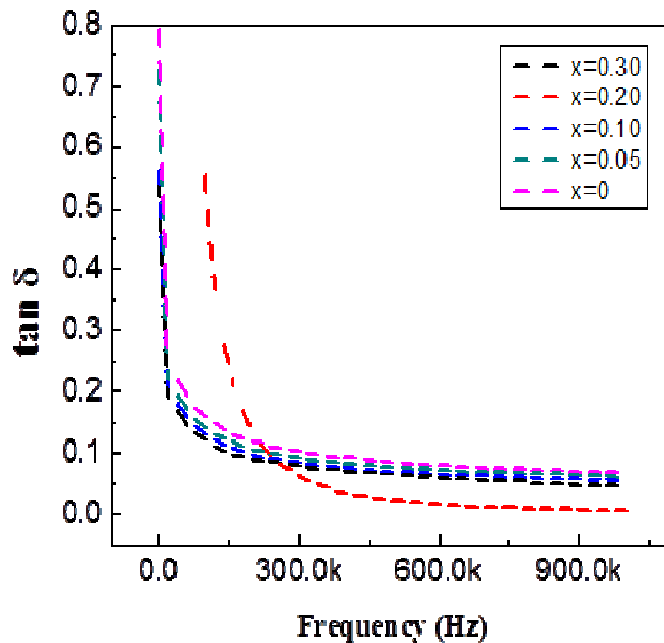
Fig. 3 Dielectric tangent loss plotted as a function of frequency

The magnetic hysteresis (M-H) loops of all the five samples are shown in Fig. 4. The loops reveal that all the samples show the saturation magnetization below 15000 G. With increasing x, the saturation magnetization, remanent and coercive filed has been increased but an anomaly occurs for 0.1% doping of lead where the magnetization, remanent and coercive field decreases. Further doping of the Pb (x = 0.2, 0.3) increases these parameters again. This non-monotonic reliance of magnetization on x shows the probability of tuning the magnetic ordering in BFO by composition adjustment during co-doping.

The main cause of net magnetization in $La_{0.1}Bi_{1-x}Pb_xFeO_3$ (x = 0.0, 0.05, 0.10, 0.20, 0.30) can be attributed to the following mechanisms. First, the diamagnetic ion (Pb^{2+}) doping seems to create oxygen vacancies and/or Fe^{4+} ions in the BFO ceramics. As the superexchange interactions for both Fe^{3+} - O - Fe^{3+} and Fe^{3+} - O - Fe^{4+} are antiferromagnetic, so they give zero net magnetization (Khomchenko 2007, 2008). Ederer *et al* (Ederer 2005) has proposed that oxygen vacancies are not able to affect the canting of the magnetic moments and hence could not enhance net magnetization. Secondly, the A-site doping can change the anisotropy constant and becomes a cause to change the spin structure of BFO from spatially modulated spin structure to a homogeneous canted one (Wang 2005). Therefore, it is likely that the structural distortion has canted the antiferromagnetic spins and induced net magnetization in our samples. The La doping changes the structure of BFO from rhombohedral to pseudotetragonal whereas, Pb doping changes its structure to pseudocubic. Further,

these doping suppress the spin structure in opposite to each other and when doping of La and Pb are equal they may the cancel the effect of each other resulting in reduction in the Latent magnetization (Ge 2012). This is the cause of low magnetization and remanance at 0.1% Pb doping. At 0.3% Pb doping the structure transforms from rohmbohedral to pseudocubic is almost complete and destroy the spatial spin structure (Zhang 2009) due to which we get large latent magnetization as compared to other samples.
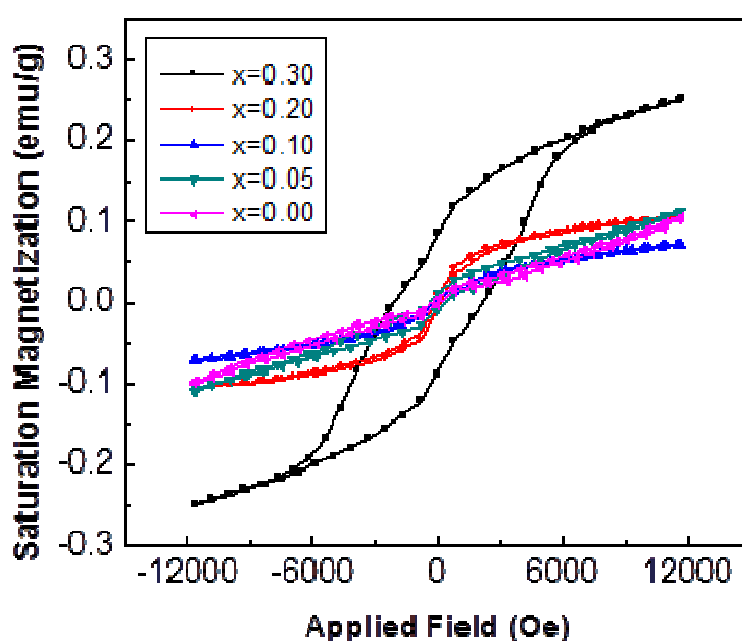

Fig. 4   Magnetic hysteresis loops of $La_{0.1}Bi_{1-x}Pb_xFeO_3$ (x = 0.0, 0.05, 0.1, 0.2, 0.3) samples

CONCLUSIONS

The effect of Pb (A-Site diamagnetic ion) doping on the crystal structure, magnetic and dielectric properties of $La_{0.1}Bi_{0.90}FeO_3$ has been studied. The $La_{0.1}Bi_{1-x}Pb_xFeO_3$ (x = 0.0, 0.05, 0.10, 0.20, 0.30) samples were prepared by sol-gel auto-combustion method. The XRD analysis reveals that all the samples have single phase perovskite structure which can be described by space group R3c. The crystallite size and unit cell volume increases with Pb doping. The Pb doping in LBFO has proved to suppress the spiral spin structure to a canted spin structure by enhancing its net magnetization but this is non-monotonical with respect to increasing x. The frequency dependent dielectric anomaly is due to the dielectric relaxation whereas the increase in dielectric factors with rising temperature is related to thermally induced enhancement of the hopping conduction.

Acknowledgements

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