



## Effect of Pb-doping on dielectric properties of BiFeO<sub>3</sub> ceramics

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### ARTICLE INFO

#### Article history:

Received 16 June 2008

Accepted 21 July 2008

Available online 28 November 2008

#### PACS:

77.65.-j

77.80.-e

75.80.+q

#### Keywords:

Ceramics

Dielectric properties

Ferroelectricity

### ABSTRACT

Pb-doped BiFeO<sub>3</sub> powders were synthesized by simultaneous precipitation method and their dielectric and ferroelectric properties were investigated after sintering in air. Bulk densities up to 93% of theoretical density can be achieved with Pb-doping. The dielectric and ferroelectric properties also improved significantly with respect to pure BiFeO<sub>3</sub> after Pb-doping.

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### 1. Introduction

The multiferroics with a coupling of at least two of the possible three orders (or degrees) of freedom viz., ferromagnetic (or antiferromagnetic), ferroelectric (or antiferroelectric), and ferroelastic are rare in nature as transition metal ions with active *d* electrons tend to reduce the off-center distortion necessary for ferroelectricity [1]. The co-existence of ferroelectricity and ferromagnetism and their coupling with elasticity provide an extra degree of freedom in the design of new functional sensors and multistate devices [2]. BiFeO<sub>3</sub> is the most interesting in the family of a very few single-phase multiferroics because of its high phase transition temperatures (Curie temperature ~1083 K and Neel temperature ~675 K) [3].

The major difficulties of making BiFeO<sub>3</sub> ceramics are: (i) synthesizing phase pure material, (ii) achieving sintered densities above 90% of theoretical density and (iii) getting highly resistive BiFeO<sub>3</sub> ceramics with low leakage current.

Several techniques have been employed in synthesizing BiFeO<sub>3</sub>. In the solid state route [4] Bi<sub>2</sub>O<sub>3</sub> and Fe<sub>2</sub>O<sub>3</sub> are reacted at a temperature in the range of 800–830 °C and unreacted Bi<sub>2</sub>O<sub>3</sub>/Bi<sub>2</sub>Fe<sub>4</sub>O<sub>9</sub> phases are removed by washing in HNO<sub>3</sub>. Another technique is simultaneously precipitaton [5], where a solution of bismuth

nitrate and iron nitrate is treated with ammonium hydroxide to get a hydroxide precipitate. The precipitate needs calcination at a temperature in the range of 550–750 °C to get phase pure BiFeO<sub>3</sub>. In another approach nanosized BiFeO<sub>3</sub> particles have been prepared by a solution evaporation (tartaric acid template) [6] technique at a temperature as low as 450 °C. Mazumder et al. [7] prepared BiFeO<sub>3</sub> through co-precipitation (700 °C), sonochemical (450 °C) and autocombustion (400 °C) routes and reported the results of a comprehensive study of the phase transition at *T<sub>N</sub>* (Neel temperature) as a function of particle size.

Incidentally, there are only a few reports of making densified and highly resistive BiFeO<sub>3</sub> ceramics. Mahesh Kumar et al. [8] reported the dielectric and ferroelectric properties of BiFeO<sub>3</sub> ceramics where BiFeO<sub>3</sub> was prepared by solid state route and there was no report about the bulk densities of the samples. The spontaneous polarization of the sample was very low. Wang et al. [9] showed that a rapid liquid-phase sintering of BiFeO<sub>3</sub> can result in 92% of relative density and gave rise to spontaneous and remanent polarization of 8.9, 4.0 μC/cm<sup>2</sup>, respectively. Pradhan et al. [10] followed similar rapid phase sintering, but the percent densification was not reported. In the later case, the spontaneous and remanent polarizations were only 3.5 and 2.5 μC/cm<sup>2</sup>, respectively instead of earlier reported [9] high values. Recently, Yuan et al. [11] followed rapid phase sintering technique and synthesized highly resistive and dense (92% of theoretical density) sample by varying the particle size of precursors Bi<sub>2</sub>O<sub>3</sub> and Fe<sub>2</sub>O<sub>3</sub> and they reported high spontaneous polarization of their samples.

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In an attempt to get improved properties, there are also a few reports on doped BiFeO<sub>3</sub>. Li et al. [12] reported the crystal structure, electronic structure and magnetic properties of Sr-doped BiFeO<sub>3</sub>. Sr-doping increases the oxygen vacancy concentration and Bi<sub>1-x</sub>Sr<sub>x</sub>FeO<sub>3</sub> behaves like an antiferromagnet and weak ferromagnet simultaneously. Palkar [13] studied the effect of Mn doping on structural, ferroelectric and magnetic properties of La-modified BiFeO<sub>3</sub>. Ferroelectric properties were not affected by Mn substitution but a small enhancement in magnetization was observed. Jun et al. [14] prepared highly resistive BiFeO<sub>3</sub> ceramics by Nb-doping and studied their electric and magnetic properties. They reported a very low remanent polarization of 0.15 μC/cm<sup>2</sup>. Jiang et al. [15] prepared La-doped BiFeO<sub>3</sub> by Pechini method followed by conventional sintering. The dissipation factor reduced to 1%, which is highly desired for potential applications. However, the reported polarization value was very low and the microstructure revealed appreciable porosity.

In this communication, we present the dielectric and ferroelectric properties of Pb-doped BiFeO<sub>3</sub> and report that lead doping in BiFeO<sub>3</sub> improves the densification behavior and dielectric and ferroelectric properties.

## 2. Experimental

Pure and Pb-doped BiFeO<sub>3</sub> (Bi<sub>1-x</sub>Pb<sub>x</sub>FeO<sub>3</sub>, x = 0.03–0.07) powders were synthesized using simultaneous precipitation route as described below. Fe(NO<sub>3</sub>)<sub>3</sub> and Bi(NO<sub>3</sub>)<sub>3</sub> solutions of 0.2 M concentration were added together and a calculated amount of Pb(NO<sub>3</sub>)<sub>2</sub>·5H<sub>2</sub>O was poured into it and stirred to get a clear solution. The mixed solution was poured into aqueous ammonia under stirring and the pH was maintained at 9 for complete precipitation. The precipitate was filtered, dried at 100 °C in an oven for 6 h and calcined at 700 °C/1 h. Pellets from the synthesized powders were prepared using uniaxial pressing at a pressure of 170 MPa. The pellets were sintered at 830 °C/2 h at a heating rate of 150 °C/h and cooled inside the furnace.

The phase identification of the sintered and ground pellets was performed on an X-ray diffractometer (Philips, PW 1710; Cu Kα radiation). The DSC study was carried out on a PerkinElmer Diamond DSC over a temperature range of 27–550 °C. The densities of the sintered pellets were measured by Archimedes' principles. For dielectric and resistivity measurements, the surfaces of the sintered pellets were ground and polished followed by application of a silver conducting paste on two opposite surfaces of the sample. The silver paste was cured at 520 °C for 15 min. Dielectric measurements were performed at room temperature using a Solartron impedance analyzer (SI 1260) in the frequency range of 100 Hz–1 MHz. Two-probe electrical resistance was measured on an HP 4339B High Resistance Meter at room temperature. Ferroelectric hysteresis loops were measured using an LC precision ferroelectric tester.

## 3. Results & discussion

Fig. 1 shows the XRD patterns of pure BiFeO<sub>3</sub> and Bi<sub>1-x</sub>Pb<sub>x</sub>FeO<sub>3</sub> (x = 0.03, 0.05 and 0.07) samples. No impurity phase or excess PbO phase was detected up to x = 0.05. For x = 0.05, small amounts of Bi<sub>2</sub>Fe<sub>4</sub>O<sub>9</sub> and Bi<sub>2</sub>O<sub>3</sub> were formed as impurity phases.

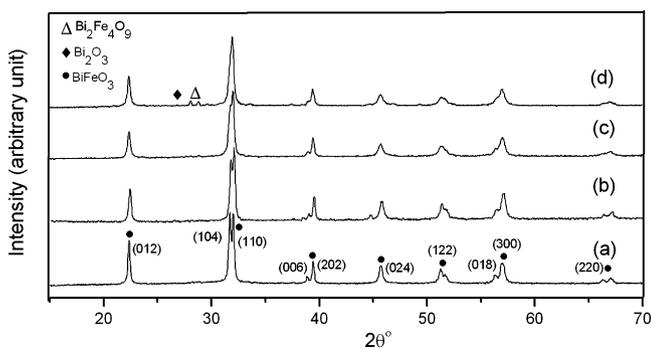


Fig. 1. X-ray diffraction patterns of (a) BiFeO<sub>3</sub>, (b) Bi<sub>0.97</sub>Pb<sub>0.03</sub>FeO<sub>3</sub>, (c) Bi<sub>0.95</sub>Pb<sub>0.05</sub>FeO<sub>3</sub>, and (d) Bi<sub>0.93</sub>Pb<sub>0.07</sub>FeO<sub>3</sub>.

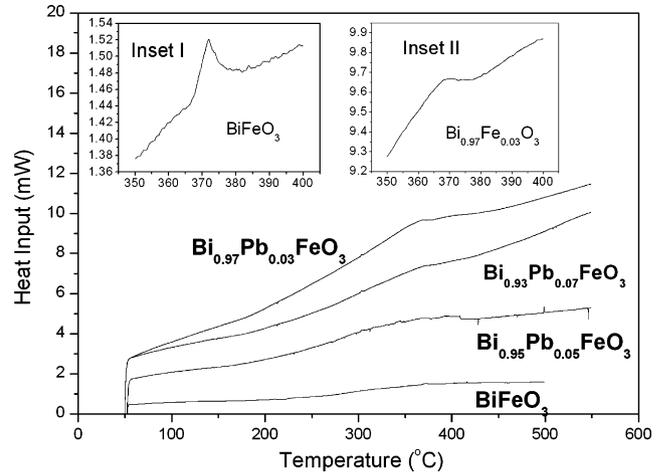


Fig. 2. DSC curves for BiFeO<sub>3</sub> and different Pb-doped BiFeO<sub>3</sub> samples. Inset I shows a sharp endothermic peak for BiFeO<sub>3</sub>. Inset II shows a broad feature for Bi<sub>0.97</sub>Pb<sub>0.03</sub>FeO<sub>3</sub>.

From DSC study, we found that pure BiFeO<sub>3</sub> showed a sharp endothermic peak (Fig. 2) corresponding to antiferromagnetic to paramagnetic transition at 373 °C, but with Pb addition there was no sharp transition. The absence of a sharp peak and a broad transition point out towards local inhomogeneity, probably in the nanoscale [7].

Fig. 3 shows the variation of bulk densities of the sintered pellets with Pb addition. In the present study, the maximum in density (~93.5%) was achieved for x = 0.05. Further addition of Pb (x = 0.07) lowered the bulk density. Fig. 4 shows the microstructure of the fracture surfaces of different Pb-doped samples. Interestingly, with Pb-doping the grain size decreased drastically. Probably, Pb-doping, up to a certain level, inhibits grain growth and helps in densification. Fig. 5 shows the variation of dielectric constant of different samples with frequency. It is clear from the figure that Pb-doping drastically reduces the frequency dispersion of BiFeO<sub>3</sub> and it is minimum for Bi<sub>0.95</sub>Pb<sub>0.05</sub>FeO<sub>3</sub> sample. In addition, Fig. 6 shows that Pb incorporation up to x = 0.05 lowers the dissipation factor at low frequencies. With further Pb-addition (which contains an impurity phase) the dissipation at low frequencies increases. To understand this behavior, we have to first note that in BiFeO<sub>3</sub>, small amounts of Fe<sup>2+</sup> ions and oxygen vacancies exist [16]. Incidentally, BiFeO<sub>3</sub> shows p-type conductivity [17], which can be understood by considering the substitution of a small amount Fe<sup>2+</sup> ions in Fe<sup>3+</sup> positions (acceptor doping of Fe<sup>3+</sup> by Fe<sup>2+</sup>). When PbO is added

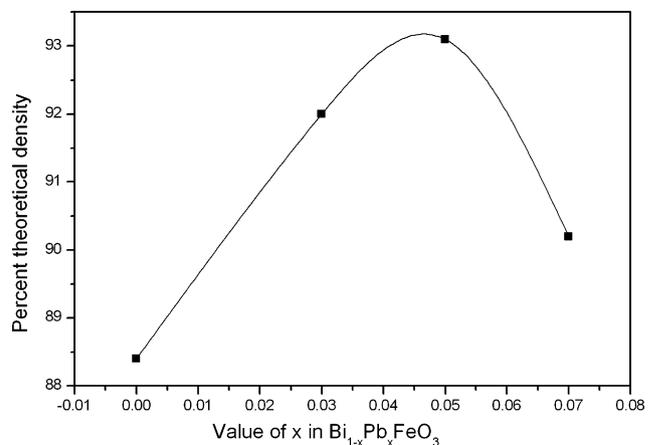


Fig. 3. Variation of sintered density with the amount of Pb-doping.

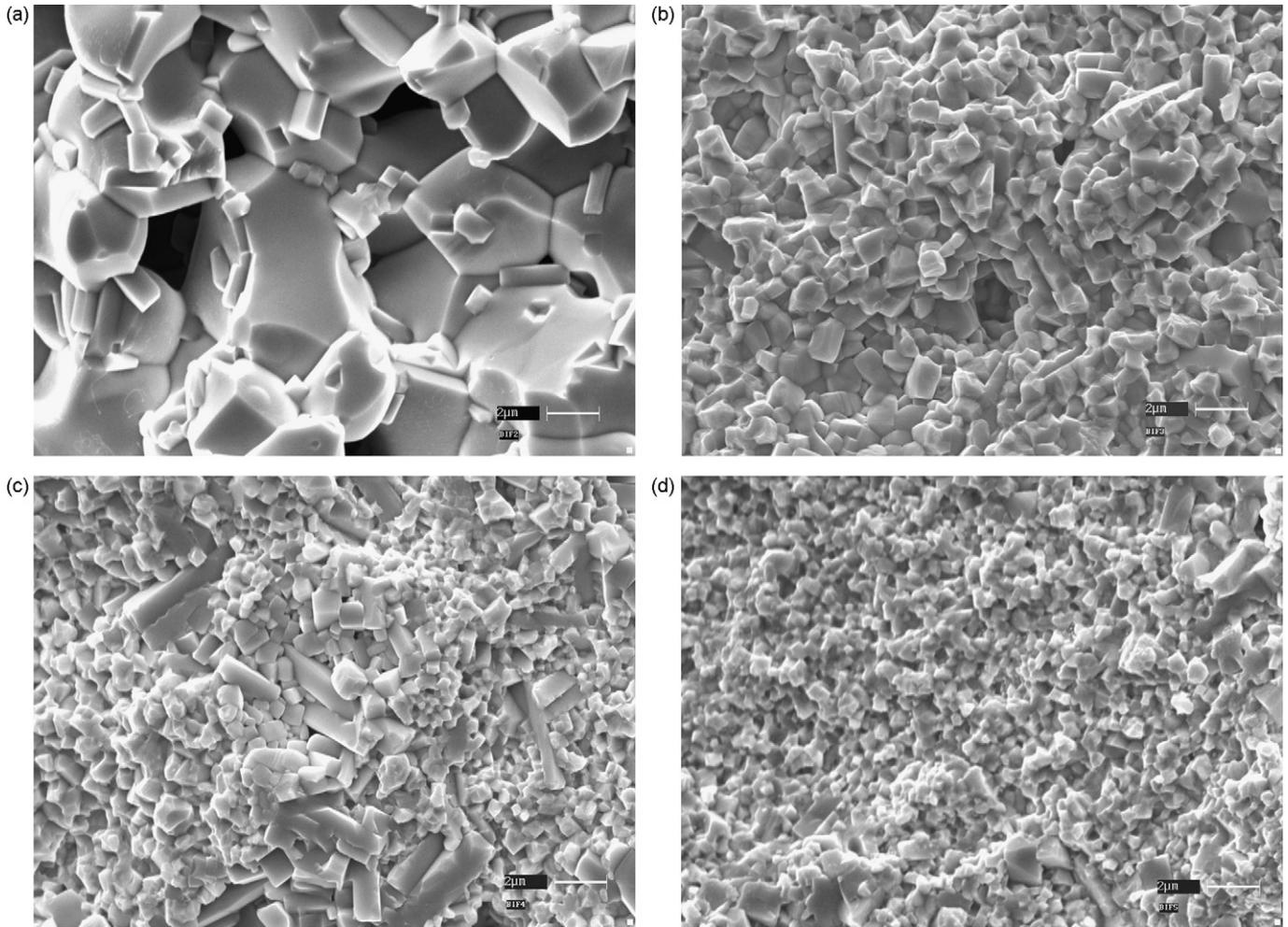


Fig. 4. SEM micrographs of fracture surfaces of (a) BiFeO<sub>3</sub>, (b) Bi<sub>0.97</sub>Pb<sub>0.03</sub>FeO<sub>3</sub>, (c) Bi<sub>0.95</sub>Pb<sub>0.05</sub>FeO<sub>3</sub>, and (d) Bi<sub>0.93</sub>Pb<sub>0.07</sub>FeO<sub>3</sub>.

to BiFeO<sub>3</sub>, Pb<sup>2+</sup> is supposed to substitute Bi<sup>3+</sup> because of the close ionic radii of Pb<sup>2+</sup> and Bi<sup>3+</sup>. Such acceptor doping of Bi<sup>3+</sup> (Bi<sub>2</sub>O<sub>3</sub>) by Pb<sup>2+</sup> (PbO) is expected to generate oxygen vacancies without the liberation of electrons [18] as given below:

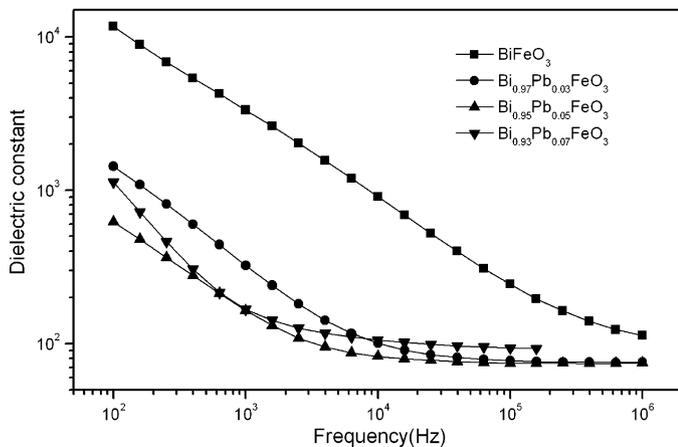


Fig. 5. Variation of dielectric constant with frequency (at room temperature) for pure and different Pb-doped BiFeO<sub>3</sub> samples.

Normally, the oxygen partial pressure in the ambience is sufficient to incorporate oxygen into the structure to nullify the oxygen vacancies and show p-type conductivity as depicted below:

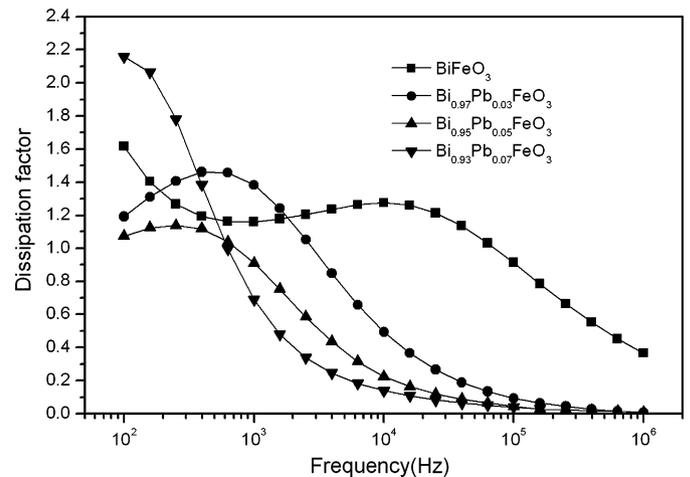


Fig. 6. Variation of dissipation factor with frequency (at room temperature) for pure and different Pb-doped BiFeO<sub>3</sub> samples.

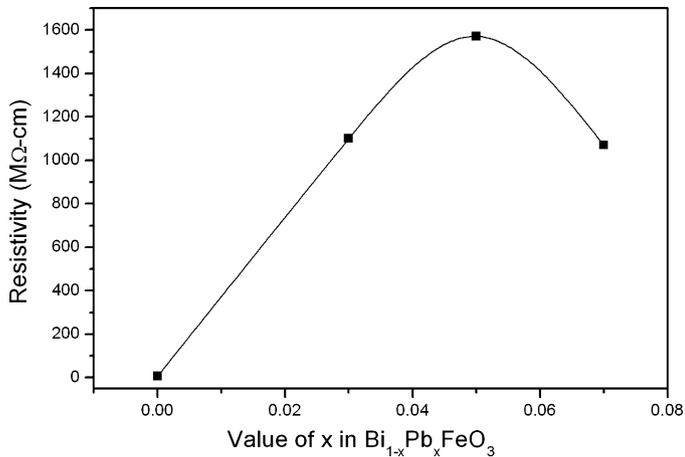
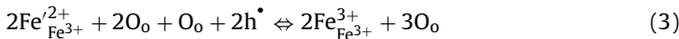


Fig. 7. DC resistivity of BiFeO<sub>3</sub> samples as a function of Pb-doping at room temperature.

The hole generated can be initially consumed by Fe<sup>2+</sup> (in Fe<sup>3+</sup> position) as given below:



resulting in lower acceptor doping of Fe<sup>3+</sup> by Fe<sup>2+</sup> in BiFeO<sub>3</sub> with consequent decrease in conductivity. However, with the increase in Pb-doping, the hole concentration should again rise because the hole compensation by the conversion of Fe<sup>2+</sup> to Fe<sup>3+</sup> (Eq. (3)) is limited by the presence of a small amount of Fe<sup>2+</sup> in BiFeO<sub>3</sub>.

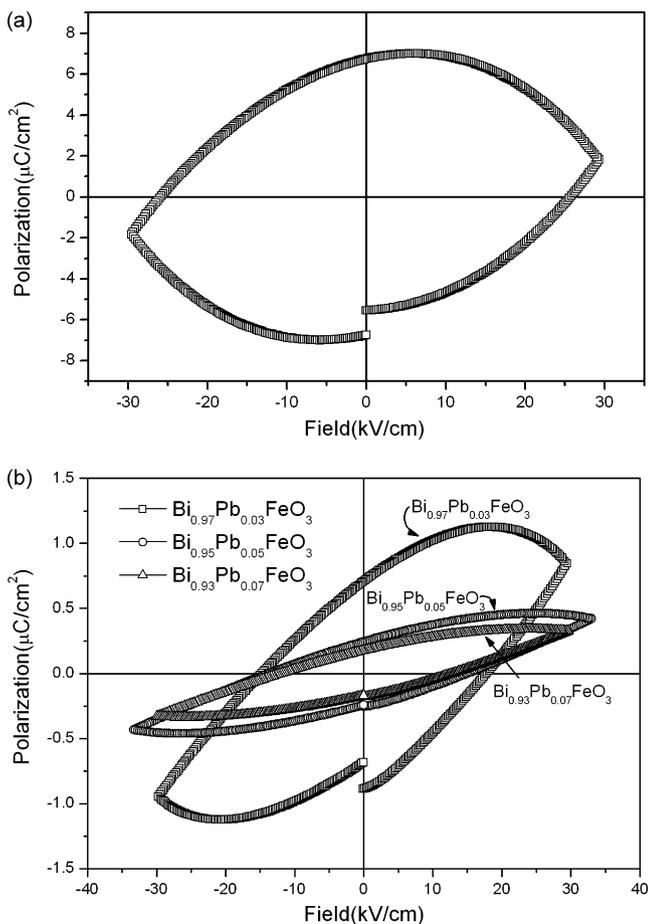


Fig. 8. P–E hysteresis loops of (a) undoped and (b) Pb-doped BiFeO<sub>3</sub> samples.

Our argument is corroborated by Fig. 7, where the resistance of BiFeO<sub>3</sub> initially increases with Pb-doping and after a certain percentage of lead addition the resistance starts falling. The dissipation factor also shows a somewhat similar trend (like the resistance values of the samples) with Pb-doping indicating the primary role of carrier-mediated loss in this system. The dissipation at low frequencies indicates Maxwell–Wagner relaxation [19] due to quasi-mobile carriers (holes in the present case). The lower dielectric constant of lead doped BiFeO<sub>3</sub> compared to pure BiFeO<sub>3</sub> can be attributed to higher space charge polarization for latter one. Fig. 8 shows the P–E loops of the pure and doped BiFeO<sub>3</sub> ceramics. Pure BiFeO<sub>3</sub> shows a lossy loop. The Pb addition increases the electrical resistivity and with increased lead doping, BiFeO<sub>3</sub> ceramics show typical non-lossy ferroelectric hysteresis loops. The apparent spontaneous polarization (as the loop is lossy) value was about 0.4 μC/cm<sup>2</sup> for Bi<sub>0.95</sub>Pb<sub>0.05</sub>FeO<sub>3</sub> which is much higher than reported earlier for pure BiFeO<sub>3</sub> (0.12 μC/cm<sup>2</sup> (lossy loop) [8]) and even for La-doped BiFeO<sub>3</sub> (0.15 μC/cm<sup>2</sup> (lossy loop) field [15]) ceramics. However, Pb<sup>2+</sup> doped samples could not reach the state of saturated polarization before the leakage current became significant.

#### 4. Conclusion

Bi<sub>1-x</sub>Pb<sub>x</sub>FeO<sub>3</sub> ceramics have been prepared by a simple simultaneous precipitation technique followed by the conventional sintering process. The sintered density and dielectric property improved with Pb addition. Typical non-lossy ferroelectric loops (in contrast to lossy loop of BiFeO<sub>3</sub>) have been observed in the Bi<sub>1-x</sub>Pb<sub>x</sub>FeO<sub>3</sub> ceramics at room temperature.

#### Acknowledgements

One of the authors (R.M.) is thankful to CSIR, India for financial support. The authors thank P.S. Mondal and P. Chowdhury of CGCRI for rendering help in carrying out this work. The authors thank D. Bhattacharya for carrying out DSC measurements and for some useful discussion. We also thank the Director of CGCRI for giving permission to publish this paper.

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