

Improved dielectric and ferromagnetic properties in Fe-doped PbTiO_3 nanoparticles at room temperature

K. C. Verma,^{1,a)} R. K. Kotnala,² and N. S. Negi¹

¹Department of Physics, Himachal Pradesh University, Shimla-171005, India

²National Physical Laboratory, New Delhi-110012, India

(Received 10 January 2008; accepted 14 March 2008; published online 16 April 2008)

Fe-doped PbTiO_3 nanoparticles have been synthesized by chemical route using polyvinyl alcohol as a surfactant. The results indicate that the dielectric constant and magnetization value of these nanoparticles depends upon their size and Fe dopants. The x-ray diffraction analysis, and transmission and scanning electron microscopies show that the particle's sizes in the specimens lie in the range of 19–30 nm. It is observed that the magnetization is enhanced with reduction in particle size. The largest value of saturation magnetization ($M_s=41.6 \times 10^{-3}$ emu/g) is observed for 1.2 mol % Fe dopants. Dielectric constant and dielectric losses are controlled up to 15 MHz at room temperature. © 2008 American Institute of Physics. [DOI: 10.1063/1.2906359]

In recent years, multiferroics have attracted a lot of attention because of their potential applications in new types of storage media using both magnetic and electric polarization. The combination of both ferroelectric and ferromagnetic properties in a single material is also interesting and fascinating.^{1,2} However, there are very few materials that can exhibit both magnetization and electric polarization. Among these, BiFeO_3 is the most extensively studied compound and is the only material known to exhibit magnetic and ferroelectric order at room temperature.³ The major problem with BiFeO_3 is its low electrical resistivity which limits the application of its ferroelectric order.^{4,5} In general, a material with a large magnetoelectric effect at room temperature is required for various device applications such as spintronics,⁶ data-storage media,⁷ and multiple-state memories.⁸ However, magnetoelectric effect of most materials is small at room temperature and, also, it is difficult to synthesize a material with large magnetoelectric effect at room temperature. Thus, the search for single-phase materials having a magnetoelectric effect at or above room temperature is going on. Recently, a few studies focusing on the Fe-doped PbTiO_3 system have shown a promising magnetoelectric effect for this material. Palkar and Malik⁹ reported the conversion of a ferroelectric PbTiO_3 to a magnetoelectric system by partially substituting Ti with Fe. Ren *et al.*¹⁰ observed room temperature ferromagnetism in Fe-doped PbTiO_3 nanocrystals prepared by hydrothermal method using polyethylene glycol as a surfactant. However, further improvement in magnetic properties of Fe-doped PbTiO_3 is required to realize its actual use in magnetoelectric device applications.

In this letter, we report the synthesis of Fe-doped PbTiO_3 nanoparticles $\text{Pb}(\text{Fe}_x\text{Ti}_{1-x})\text{O}_3$ by a chemical route using polyvinyl alcohol (PVA) as a surfactant. Starting materials were lead acetate, tetra-*n*-butyl orthotitanate and ferric chloride. Tetra-*n*-butyl orthotitanate ($\text{C}_{16}\text{H}_{36}\text{O}_4\text{Ti}$) was added in a solution of ethyl alcohol and acetic acid (75:25). Lead acetate solution in distilled water was mixed with the above solution and was allowed for constant stirring for 3 h. Ferric

chloride was added to the resultant mixture. PVA was also added to act as a surfactant to encapsulate the cationic species in divided groups during chemical reaction. The final solution appeared as a clear gel at room temperature. The gel was dried at 300 °C and heated at 700 °C for 3 h to crystallize the specimen. The structural and microstructural properties of the Fe doped PbTiO_3 particles were characterized by using x-ray diffraction (XRD) and transmission/scanning electron microscopes (TEM/SEM) (Hitachi H-7500/JEOL JSM6100), respectively. Magnetization measurements were performed at room temperature using a vibrating sample magnetometer (VSM-735). For electrical measurements, heat-treated powder particles were pressed into pellet by applying pressure of 4 bar for 10 min. The specimens were then sintered at higher temperature ~ 1000 °C for 5 h. The dielectric properties of sintered pellets were measured by using a LCR meter (Agilent 4285A) in the higher frequency range of ~ 0.75 –25 MHz. The variation of dc resistivity with different Fe contents was measured using a Keithley 2611 system.

Figure 1(a) shows the XRD patterns of PbTiO_3 powder samples doped with different Fe concentrations and heated at 700 °C. It is found that all Fe-doped PbTiO_3 compounds are single-phase materials crystallizing in the same structure as that of parent PbTiO_3 with minor pyrochlore $\text{Pb}_2\text{Ti}_2\text{O}_6$ as an impurity phase. The similar impurity phase is also observed in the system by Palkar and Malik.⁹ The tetragonal distortion (c/a) is decreased, whenever Fe content increases from 0 to 4 mol % in PbTiO_3 . This may be understood because of reduction in lattice distortion on Fe doping at Ti site. The mean particle size in the specimens was calculated by Scherrer's equations.¹¹ Particle's sizes are summarized in Table I. The results show that the average particle size in the specimens lie in the range of 19–30 nm. The comparative XRD patterns of two specimens i.e., with 0.6 and 4 mol % Fe doped at higher and lower sintering temperature are presented in Fig. 1(b). It was observed that impurity phase in these specimens completely disappears at higher sintering temperature of ~ 1000 °C. Similar results were also found in other specimens. It is observed that the particle size in specimen 2 increases from 30 to 35 nm at higher sintering temperature as calculated by Scherrer's equations. Similarly, in

^{a)} Author to whom correspondence should be addressed. Tel.: +91 0177 2830950. FAX: +91 0177 2830775. Electronic mail: kuldeep0309@yahoo.co.in.

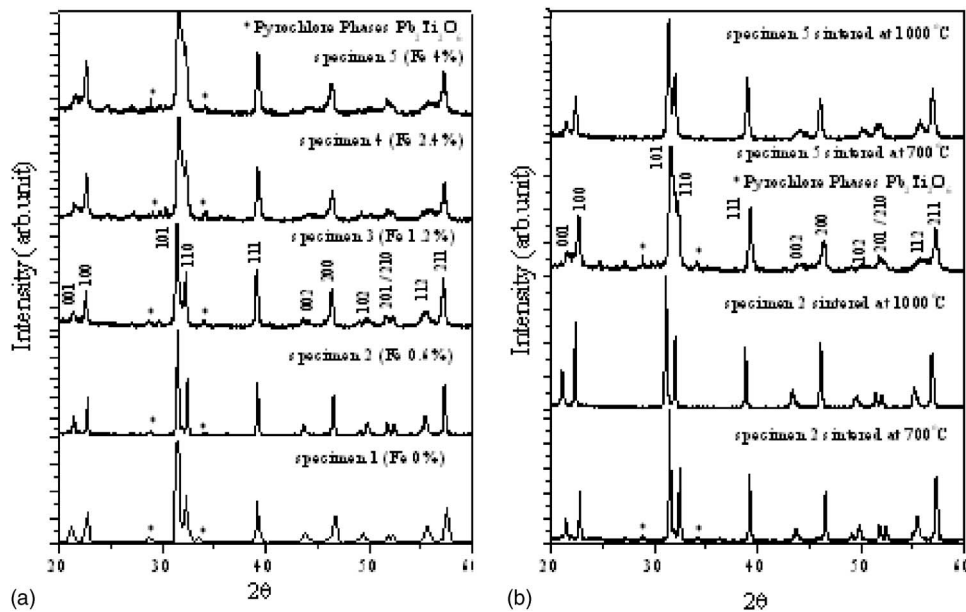


FIG. 1. (a) XRD of powder samples heated at 700 °C. (b) Comparative XRD patterns of powder (heated at 700 °C) and pellet (sintered at 1000 °C).

specimen 5, it increases from 19 to 22 nm. Thus, the grain sizes in the sintered specimens (~ 1000 °C) still lie in the range of nanometer. Two typical micrographs for specimen 2, i.e., TEM for specimen heated at 700 °C and SEM for specimen sintered at ~ 1000 °C are shown in Figs. 2(a) and 2(b). The values of particle size, as obtained from TEM/SEM images, agree with the one that calculated from XRD patterns.

The room temperature hysteresis loops of the Fe-doped PbTiO_3 nanoparticles with different Fe content are presented in Fig. 3. An anti- S -type magnetization-field (M - H) curve is obtained for undoped specimen, which confirms the intrinsic diamagnetism in pure PbTiO_3 . The M - H curve gradually transfers into the S -type hysteresis loop on increasing the Fe-doping concentration. When the Fe concentration is 0.6%, a typical ferromagnetic hysteresis loop appears with saturation magnetization $M_s \approx 6.7 \times 10^{-3}$ emu/g ($0.086 \mu_B/\text{Fe}$) and coercive field $H_c \sim 550$ Oe. The ferromagnetism in Fe-doped PbTiO_3 nanoparticles further improves on increasing Fe content to 1.2 mol %. We have observed $M_s \approx 41.6 \times 10^{-3}$ emu/g ($0.52 \mu_B/\text{Fe}$) and $H_c \sim 125$ Oe for the specimen. The observed value of saturation magnetization is significantly higher than $M_s \approx 0.8 \times 10^{-3}$ emu/g ($0.01 \mu_B/\text{Fe}$) reported by Ren *et al.*¹⁰ for their hydrothermal processed Fe doped nanocrystals ~ 100 nm using polyethylene glycol (PEG) as a surfactant. Improvement in ferromagnetic properties is due to the smaller particle's sizes in our specimens. This is a typical behavior of nanosized magnetic material where magnetization increases with reduction in particle size. In nanosized magnetic material, superparamagnetic

relaxation contributes least to the hysteresis than ferromagnetic.¹² It has been reported by Mu *et al.*¹³ that PVA as a surfactant is more efficient in surface modification and reducing particle size than PEG. Therefore, small particle sizes observed in our specimens may be attributed to the effect of PVA surfactant. In addition, surface modification can significantly influence the properties of nanoparticles including particle size, size distribution, and particle morphology. The well-defined M - H curves confirm that specimens with 0.6 and 1.2 mol % Fe are ferromagnetic at room temperature. With further increase in Fe concentration from 1.2% to 4% in PbTiO_3 , S -type M - H curve gradually linearize. The less saturated hysteresis loops with linearization in later composition of Fe-doped PbTiO_3 nanoparticles indicate that they are basically paramagnetic with weak ferromagnetism. The appearance of strong paramagnetism in these specimens is due to the dominant paramagnetic contribution of Fe^{3+} ions at $\text{Fe} > 1.2$ mol %. On other hand, strong ferromagnetism in specimens with 0.6 and 1.2 mol % Fe is due to the F -center exchange mechanism in $\text{Fe}^{3+} - \text{V}_\text{O}^{2-} - \text{Fe}^{3+}$ groups.^{6,14}

Figure 4(a) shows the variation of dielectric constant (ϵ') as a function of frequency for these specimens with and without Fe doping. It can be observed in Fig. 4(a) that the dielectric constant of specimen without Fe content shows a

TABLE I. Properties of Fe-doped nanoparticles.

| Specimen no. | c/a ratio | Particle size (nm) | ϵ' at 1 MHz | ϵ' at 15 MHz | M_s (10^{-3} emu/g) |
|--------------|-------------|--------------------|----------------------|-----------------------|--------------------------|
| 1 | 1.064 | 24 | 117 | Resonance | Diamagnetic |
| 2 | 1.061 | 30 | 28 | 35 | 6.89 |
| 3 | 1.058 | 24 | 48 | 49 | 41.60 |
| 4 | 1.056 | 25 | 39 | 53 | 2.47 |
| 5 | 1.055 | 19 | 35 | 54 | Paramagnetic |

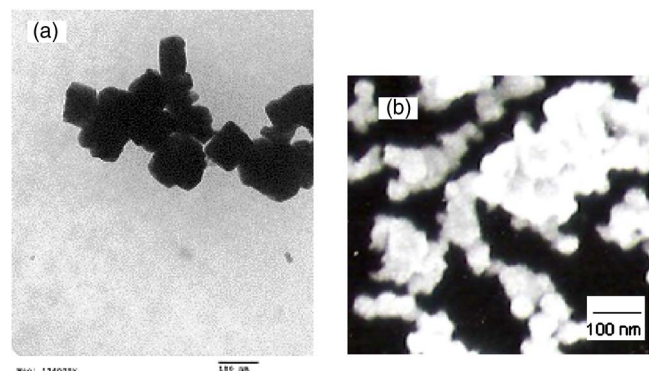


FIG. 2. (Color online) (a) TEM for specimen 2 heated at 700 °C. (b) SEM of pellet for specimen 2 sintered at 1000 °C.

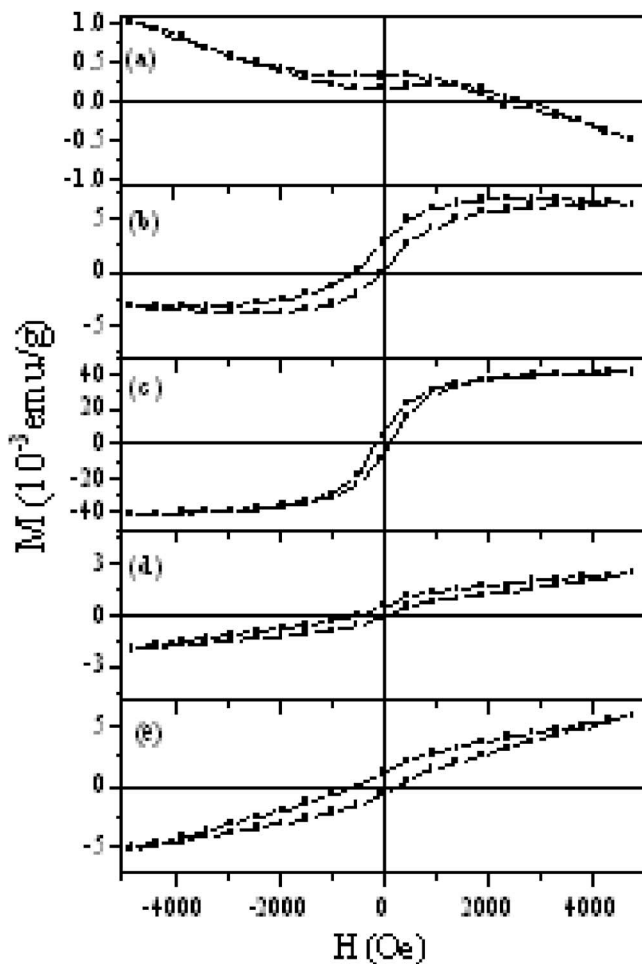


FIG. 3. M - H curves of the specimens heated at 700 °C with (a) 0% Fe, (b) 0.6% Fe, (c) 1.2% Fe, (d) 2.4% Fe, and (e) 4% Fe doping concentrations at room temperature.

strong dispersion in low frequency <100 kHz. It is possible that this dependence of dielectric constant on frequency is caused by space charge polarization. These charges can be originated during the heat treatment of the specimen. When the specimens were doped with Fe, a reduction in dispersion of dielectric constant was observed at a low frequency. This result indicates that there was a reduced space charge effect in the dielectric properties because Fe doping reduces oxygen vacancies. In doped specimens, there is no dispersion in the dielectric constant up to 15 MHz as against 3 MHz for undoped specimen. At frequency >3 MHz (undoped) and >15 MHz (Fe-doped) specimens, the dispersion in dielectric constant is due to resonance effect. The resonance may arise due to the matching of the frequency of charge transfer between the cations and anions, and that of the applied electric field. Similar inference can also be drawn from frequency dependence dielectric loss curves of these specimens [Fig. 4(b)], where specimen without Fe doping appears as more conducting in nature. Moreover, from Fig. 4(c), the resistivity of specimens increases with increasing Fe concentration. These results suggest that dielectric properties of PbTiO_3 nanoparticles improve on Fe doping.

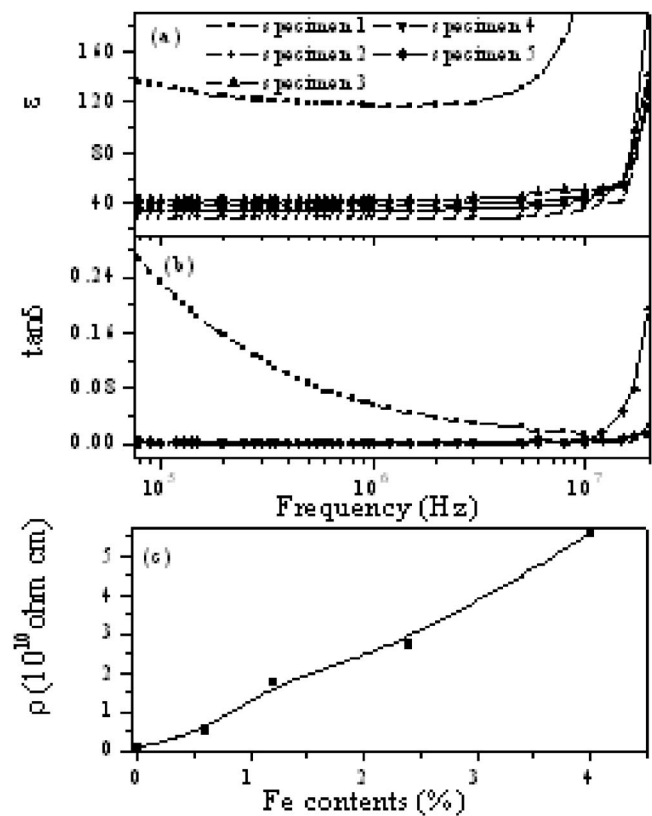


FIG. 4. (a) Variation of dielectric constant (ϵ). (b) Variation of dielectric loss ($\tan \delta$) as a function of frequency at room temperature. (c) Resistivity (ρ) with different Fe contents.

To sum up, a chemical route using PVA, which acts as an efficient surfactant to limit the particle size, can synthesize Fe-ion-doped PbTiO_3 nanoparticles. The value of particle size obtained from XRD and TEM/SEM lies in the range of 19–30 nm. Significant improvement in magnetic properties is observed in these nanoparticles with maximum value of $M_s \approx 41.6 \times 10^{-3}$ emu/g ($0.52 \mu_B/\text{Fe}$). It is concluded that the controlled dielectric properties at higher frequency and better magnetization were observed at room temperature.

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