



Intrinsic study for magnetoelectric coupling in $\text{Pb}_{1-x}\text{Sr}_x(\text{Fe}_{0.012}\text{Ti}_{0.988})\text{O}_3$ nanoparticles

Kuldeep Chand Verma^{a,*}, R.K. Kotnala^b, N.S. Negi^a

^a Department of Physics, Himachal Pradesh University, Shimla-171005, India

^b National Physical Laboratory, New Delhi-110012, India

ARTICLE INFO

Article history:

Received 11 July 2009

Accepted 19 July 2009 by A.H. MacDonald

Available online 24 July 2009

PACS:

75.80.+q

73.63.Bd

77.80.Bh

Keywords:

A. Nanostructures

B. Chemical synthesis

C. X-ray scattering

D. Phase transitions

ABSTRACT

Intrinsic magnetoelectric (ME) coupling due to anomalous phase transition temperature of multiferroic $\text{Pb}_{1-x}\text{Sr}_x(\text{Fe}_{0.012}\text{Ti}_{0.988})\text{O}_3$ (PSFT) has been studied. The average particle size of PSFT specimens was measured from X-ray diffraction peaks and scanning electron microscopy. The ferromagnetic phase transition temperature (T_{pm}) was evaluated by temperature dependent heat flow, initial permeability (μ_i) and magnetic susceptibility (χ). However, ferroelectric phase transition temperature (T_{pe}) was observed from temperature dependent relative permittivity (ϵ), and dc resistivity (ρ_{dc}). The doping of Fe in PbTiO_3 (PSFTO) has greatly reduced T_{pe} , while the doping of Sr in PSFTO has reduced T_{pm} . The higher frequency dependent dielectric constant is explained in terms of higher dc resistivity of the PSFT nanoparticles involving Variable-Range-Hopping (VRH) conduction. The observed VRH mechanism shows low value of activation energy (i.e., in the order of meV) of fermi gap giving large ME output.

© 2009 Elsevier Ltd. All rights reserved.

1. Introduction

Multiferroic magnetoelectric materials have attracted great attention due to the coexistence of ferromagnetic and ferroelectric order and open multifunctional way in new device applications [1–4]. The transition-metal-doped multiferroic systems attribute magnetoelectric behavior at room temperature because their d electrons reduce the tendency for an off-centering distortion [5]. This rareness in existing room temperature multiferroic behavior involves coupled parameters, i.e., magnetoelectric (ME) coupling. ME coupling means magnetic degree of freedom can be manipulated by an electric field and vice versa [6,7]. The ME coupling can largely be divided into two distinct categories, namely, extrinsic and intrinsic coupling. Generally, the researches have found extrinsic ME coupling by measuring either induced voltage output under the action of an external magnetic field or induced magnetization by an electric field [8,9].

On the other hand, the intrinsic ME coupling between electric polarization (P) and magnetization (M) in the absence of any probing field has been done in various multiferroic systems. According to the Landau–Devonshire theory [10], the anomalous phase transition temperature of ferroelectric (T_{pe}) and ferromagnetic (T_{pm})

behavior, causes intrinsic ME coupling. This anomaly can change magnetic moments near T_{pe} or vice versa. It is attributed in part to the symmetric spin–spin interaction within the Landau theory proposed by Mostovoy [11], that the propagation vector and the rotation axis of the helical modulation are parallel and the corresponding cross product of both vectors result to zero. In most studied multiferroic systems [12–15], the helical magnetic structure showed antisymmetric Dzyaloshinskii–Moriya spin–spin interaction, resulting antiferromagnetic (AFM) ordering temperature. The coupling between the ferroelectric order and the frustrated AFM spin structure by phase transition temperature (T_p) is difficult. Also, the value of T_{pe} appears at higher temperature because the instability occurs in the lattice due to their AFM behavior [16]. So, recently, we have developed $\text{Pb}(\text{Fe}_{0.012}\text{Ti}_{0.988})\text{O}_3$ (PFT) [4,17] and Sr-doped PFT (PSFT) nanomultiferroic systems [18] which have helical magnetic structure of parallel spins, and show good ferromagnetism and ferroelectricity at room temperature. Also, the magnetoelectric nanoparticles in these PFT and PSFT systems have small values of lattice distortion and phase transition temperature, and simultaneously large value of dc resistivity. It is observed that the intrinsic ME coupling due to simultaneous change in the T_p of both electric and magnetic behavior, may exist at lower temperature in PSFT nanoparticles.

In view of the above facts, the main aim of the present work is to evaluate simultaneous change in temperature dependent magnetic and electric behaviour of $\text{Pb}_{1-x}\text{Sr}_x(\text{Fe}_{0.012}\text{Ti}_{0.988})\text{O}_3$ (PSFT)

* Corresponding author. Tel.: +91 0177 2830950; fax: +91 0177 2830775.
E-mail address: kuldeep0309@yahoo.co.in (K.C. Verma).

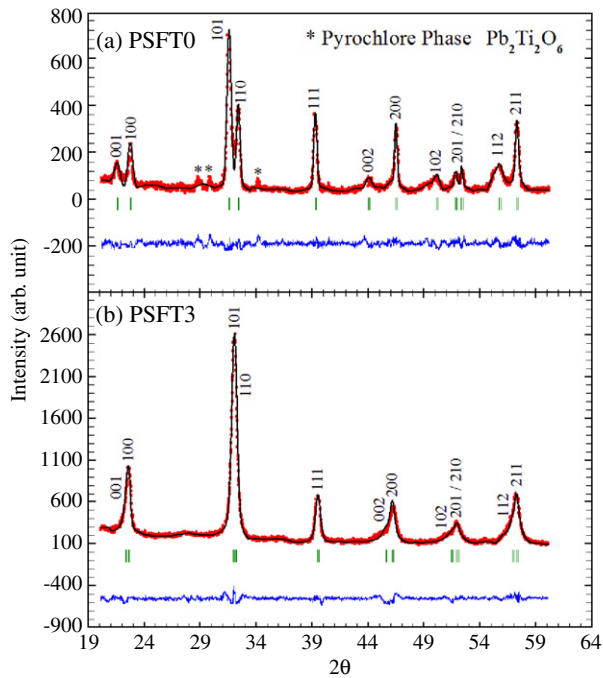


Fig. 1. Rietveld refinement of XRD data of PSFT specimens of nanoparticles heated at 700 °C for 2 h.

[$x = 0$ (PSFT0), and 0.3 (PSFT3)] nanoparticles causing intrinsic ME coupling which was given by the Landau–Devonshire theory. For this purpose, we have synthesized PSFT nanoparticles by chemical route using PVA as a surfactant. The anomalous phase transition temperatures of the PSFT specimens for electric and magnetic behavior shows intrinsic ME coupling. T_{pm} has been measured from temperature dependent heat flow (DSC measurement), initial permeability (μ_i) and magnetic susceptibility (χ). T_{pe} has been studied by temperature dependent relative permittivity (ϵ), and dc resistivity (ρ_{dc}). In these PSFT specimens, the effect of addition of Fe for Ti and Sr for Pb on T_{pe} and T_{pm} has been explained in terms of structural parameters and hopping of $Fe^{3+} \leftrightarrow Fe^{2+}$, $Ti^{4+} \leftrightarrow Ti^{3+}$ ions, respectively. The effect of PSFT nanoparticles to introduce disordered and higher frequency response in dielectric behaviour has been given by Variable-Range-Hopping (VRH) conduction mechanism. Also, the Curie–Weiss law has been used for fitting electric and magnetic phase transition temperature.

2. Experimental details

The PSFT nanoparticles have been prepared by a chemical synthesis route. The details of material processing were given elsewhere [17,18]. The phase structure and nano-behavior of PSFT specimens were carried out by X-ray diffraction (XRD) using PAN analytical X-Pert PRO system. The lattice parameters were studied by fitting XRD data with Rietveld refinement using FullProf program. The microstructures of PSFT specimens were analyzed by Scanning Electron Microscopy (SEM) using JEOL JSM 6100 system. T_{pm} has been measured from heat flow in differential scanning calorimetry (DSC) analysis (LINSEIS DSC L63), μ_i using LCR meter (Agilent: 4285A) and χ using vibrating sample magnetometer (VSM-735). T_{pe} has been determined by temperature dependent ϵ using LCR meter and ρ_{dc} using Keithley 2611 source meter.

3. Results and discussion

Analysis of XRD pattern reveals that the multiferroic PSFT specimens have tetragonal perovskite structure with minor pyrochlore

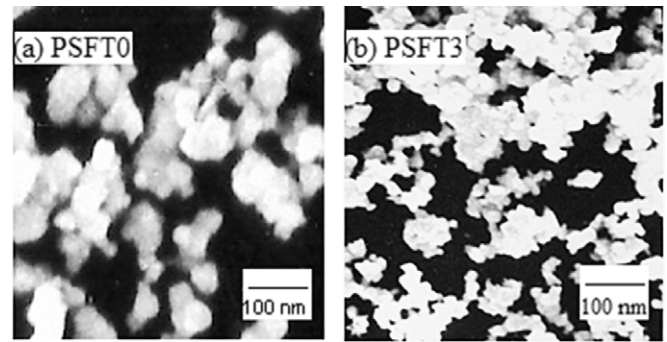


Fig. 2. SEM of PSFT specimens heated at 700 °C for 2 h.

$Pb_2Ti_2O_6$ as an impurity phase (Fig. 1). The similar impurity phase is also observed in the system by Palkar et al. [8]. The Rietveld refinement of the diffraction intensities (using FullProf program) for parent $PbTiO_3$ [19] has been used to describe the structural parameters of PSFT specimens. The refined XRD data shows tetragonal phase in PSFT0, and coexistence of tetragonal and cubic phases in PSFT3 specimens with space group $P4$ mm. The Wyckoff position (x, y, z) for Pb/Sr (1a), Ti/Fe (1b), and O (1b) and O (2c), and lattice constants, a and c are given in Table 1. The lattice distortion (c/a) reduces with Sr doping, and the observed values are 1.052(4) and 1.0031(2) for PSFT0 and PSFT3 specimens, respectively. This is based on the nature of the splitting of (001) and (100) peaks around $2\theta \sim 22^\circ$ and (101) and (110) peaks around $2\theta \sim 32^\circ$. This can be explained due to the doping of $SrTiO_3$ having perovskite cubic $Pm\bar{3}m$ structure in PFT system, which reduces the lattice distortion (c/a). The observed values of unit cell volume, R factors (reliability factors based on the Bragg intensities and the weighted profile) and χ^2 (goodness of fitting) are also given in Table 1. The lower value of unit cell volume for PSFT3 (60.87 \AA^3) as compared to PSFT0 (63.485 \AA^3) may be attributed to smaller particle size of PSFT3 (i.e., average particle size is 8 ± 1 nm) than PSFT0 (i.e., average particle size is 24 ± 1 nm) [17,18]. The average particle size was measured by using Scherrer's relation for XRD peak broadening. The nano-sized particles in the specimens result in the increase in number of grain boundaries which causes the decrease of resulting volume fraction of atoms between them. These PSFT nanoparticles also show higher values of R factors (i.e., 2.34 for PSFT0 and 2.43 for PSFT3 specimens) and χ^2 (i.e., 3.981 for PSFT0 and 4.45 for PSFT3 specimens). Fig. 2 shows the SEM micrographs of PSFT specimens. Using statistical analysis in SEM, the average particle sizes were measured as 24 ± 1 nm and 9 ± 1 nm, respectively, for PSFT0 and PSFT3 specimens.

To obtain T_{pm} of the PSFT specimens, the temperature dependent heat flow, and μ_i curves are shown in Figs. 3a and 3b. Fig. 3a represents DSC spectra of heat flow with heating rate of 5 K/min measured for PSFT specimens with different Sr concentration (0 to 30 mol%). The specimen without Sr (PSFT0) doping shows endothermic peak near 865 K which is the value of T_{pm} . However, the doping of Sr has lowered the value of T_{pm} by showing endothermic peaks at 639, 632 and 556 K, respectively, for PSFT1 (Sr = 10 mol%), PSFT2 (Sr = 20 mol%) and PSFT3 (Sr = 30 mol%) specimens. The decrease in the value of T_{pm} has further substantiated the reduction in the structural parameters (tetragonal to cubic) and particle size of PSFT specimens with Sr doping as discussed earlier. These reduced structural parameters may have short-range order effects between nearest-neighbor spins in the high-temperature phase [20]. However, 10 mol% Sr in PSFT system shows a drastic reduction in T_{pm} . In contrast slight reduction in T_{pm} is observed for PSFT with 20 mol% Sr. The significant reduction in T_{pm} is also observed for PSFT3. This type of behaviour has occurred because 10% Sr doping in $PbTiO_3$ has greatly reduced its tetragonal structure and the reduction is slight for PSFT with 20 mol% Sr [21]. PSFT with 30 mol%

Download English Version:

<https://daneshyari.com/en/article/1595148>

Download Persian Version:

<https://daneshyari.com/article/1595148>

[Daneshyari.com](https://daneshyari.com)