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2007 J. Phys.: Condens. Matter 19 242202

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## FAST TRACK COMMUNICATION

# Study of dielectric, magnetic, ferroelectric and magnetoelectric properties in the $\text{PbMn}_x\text{Ti}_{1-x}\text{O}_3$ system at room temperature

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Received 18 April 2007, in final form 4 May 2007

Published 18 May 2007

Online at [stacks.iop.org/JPhysCM/19/242202](http://stacks.iop.org/JPhysCM/19/242202)

## Abstract

We report magnetoelectric coupling at room temperature between ferroelectric and magnetic order parameters in Mn-doped  $\text{PbTiO}_3$  compounds prepared by a solid-state reaction method. X-ray diffraction showed that  $\text{PbMn}_x\text{Ti}_{1-x}\text{O}_3$  ( $x = 0.1, 0.3$  and  $0.5$ ) compounds were single phase. The Mn substitution reduced the lattice distortion, i.e., the  $c/a$  ratio, and hence the ferroelectric Curie temperature ( $T_C$ ) decreased with increasing Mn content. High-temperature magnetization measurements showed that the ferromagnetic Curie temperature ( $T_M$ ) decreases with increasing Mn in  $\text{PbMn}_x\text{Ti}_{1-x}\text{O}_3$ . An anomaly in the dielectric constant ( $\epsilon$ ) was observed in the vicinity of the ferromagnetic transition temperature. These samples exhibited magnetism and ferroelectricity simultaneously at room temperature, which was evidenced from the coexistence of saturated magnetization and polarization hysteresis loops. An enhancement in saturation polarization after poling the samples in the magnetic field was evidence of magnetoelectric coupling at room temperature. An enhancement of 11–13% in polarization was observed after poling the samples in a magnetic field at 1.2 T.

(Some figures in this article are in colour only in the electronic version)

## 1. Introduction

In recent years, considerable research attention has been focused on ferroelectromagnets or, according to modern terminology, multiferroics (materials with coexisting magnetic and electric ordering) [1]. The interaction between the electric and magnetic subsystems can manifest itself as a magnetoelectric effect, i.e., the magnetization induced by an electric field

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or the electric polarization induced by a magnetic field [2]. Magnetoelectric effects have long been a subject of academic interest. However, the recently discovered giant magnetoelectric effect [3] has opened up strong possibilities for the practical use of ferroelectromagnets for converting electric fields into magnetic fields and vice versa. This is one of the important problems in the field of sensor engineering, microelectronics, and technology for producing magnetic storage systems.

The particular interest expressed by researchers in ferroelectromagnets is explained not only by the magnetoelectric effect but also by the possibility of radically changing the properties of materials in response to electric and magnetic fields, including the induction of 'cross' phase transitions. Here, the term 'cross' means the effect of an electric field on the magnetic subsystem and, vice versa, the effect of a magnetic field on the electric subsystem of the multiferroic under consideration.

At present, extensive studies of multiferroics and the active search for new materials with the giant magnetoelectric effect continue [1, 3–9]. Recently, we have observed enhanced multiferroic properties in Ti-doped BiFeO<sub>3</sub> [10, 11]. Palkar *et al* [12] reported the conversion of ferroelectric PbTiO<sub>3</sub> into a multiferroic by partially substituting Ti with Fe, and we have shown enhanced multiferroic properties in Pb<sub>1-x</sub>Ba<sub>x</sub>(Fe<sub>0.5</sub>Ti<sub>0.5</sub>)O<sub>3</sub> system [13]. In the present work we report for the first time on Mn-doped PbTiO<sub>3</sub> compounds, PbMn<sub>x</sub>Ti<sub>1-x</sub>O<sub>3</sub>, which exhibit magnetic and ferroelectric properties, and magnetoelectric coupling at room temperature.

## 2. Experimental details

PbMn<sub>x</sub>Ti<sub>1-x</sub>O<sub>3</sub> (PMT) ceramics with  $x$  varying from 0.1 to 0.5 in steps of 0.2 were prepared by a conventional solid-state reaction method. Stoichiometric amount of high-purity PbO (with 5 wt% excess), TiO<sub>2</sub> and MnO<sub>2</sub> were weighed, and thoroughly mixed for several hours using high-purity acetone as a medium. The resultant mixture was precalcined at 900 °C for 10 h in a programmable furnace with an accuracy of ±1 °C. The calcined mixture was again ground thoroughly before heating at 950 °C for 2 h. The powders were pressed uniaxially into disc pellets of 6 mm diameter and 1 mm thickness. The final sintering of the pellets was done at 1150 °C for 2 h. The prepared samples were characterized by various techniques. The crystal structure of the sintered samples was examined with an x-ray diffractometer (Bruker D8) using Cu K $\alpha$  radiation. The dielectric measurements were made from room temperature to 500 °C in the frequency range 100 Hz–1 MHz by using an LCR meter (Model 3532-50, HIOKI). The polarization hysteresis ( $P$ – $E$ ) loop was measured by using a ferroelectric loop tracer with a standard Sawyer–Tower circuit at 50 Hz. High-temperature magnetization measurements were made on a Princeton Applied Research (Model 155) vibrating sample magnetometer (VSM). The magnetic susceptibility was measured in a magnetic field of 5 kOe from 293 to 633 K. The magnetization hysteresis ( $M$ – $H$ ) loops were evaluated using a superconducting quantum interference device (SQUID).

## 3. Results and discussion

Figure 1 shows the XRD patterns of the PMT ceramics. It can be seen that the ceramics show single-phase characteristics. Lead titanate (PbTiO<sub>3</sub>) is a displacive type of ferroelectric compound having tetragonal structure with very large lattice distortion from a cubic structure ( $c/a \sim 1.064$ ). The crystal structure of the PMT ceramics remains tetragonal like that of the parent compound (PbTiO<sub>3</sub>) even up to 50 mol% substitution of Mn for Ti. It is clear from table 1 that, with the increase in Mn concentration, the lattice parameter  $a$  increases from 3.899 to 3.918, 3.922 and 3.931 Å, while lattice parameter  $c$  decreases from 4.151 to 4.118, 4.0593

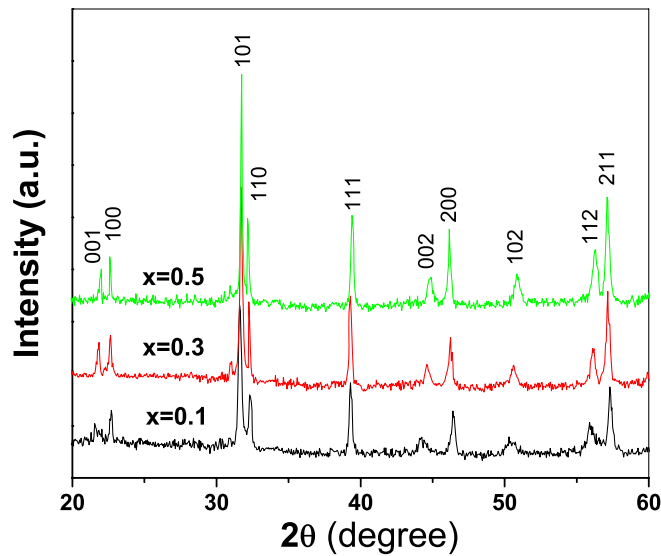


Figure 1. X-ray diffraction pattern for  $\text{PbMn}_x\text{Ti}_{1-x}\text{O}_3$  ceramics.

Table 1. Structural, electrical and magnetic parameters of  $\text{PbMn}_x\text{Ti}_{1-x}\text{O}_3$ .

Sample	Lattice constant $a$ (Å)	Lattice constant $c$ (Å)	Cell volume (Å) <sup>3</sup>	$c/a$ ratio	Ferroelectric Curie temperature ( $T_C$ ) (°C)	Ferromagnetic Curie temperature ( $T_M$ ) (°C)
$\text{PbMn}_{0.1}\text{Ti}_{0.9}\text{O}_3$	3.918	4.1118	63.1191	1.049	450	340
$\text{PbMn}_{0.3}\text{Ti}_{0.7}\text{O}_3$	3.922	4.0593	62.4405	1.035	400	320
$\text{PbMn}_{0.5}\text{Ti}_{0.5}\text{O}_3$	3.931	4.0332	62.3241	1.026	370	300

and 4.0332 Å for  $x = 0.1, 0.3$  and  $0.5$ , respectively. This results in decrease in the tetragonal ratio ( $c/a$ ) and unit cell volume, and hence the decrease in ferroelectric Curie temperatures ( $T_C$ ) of the PMT ceramics. This is as expected since the ionic radius of  $\text{Mn}^{4+}$  is smaller than that of  $\text{Ti}^{4+}$ . The unit cell parameters, tetragonal ratio and ferromagnetic and ferroelectric Curie temperatures of  $\text{PbMn}_x\text{Ti}_{1-x}\text{O}_3$  system are given in table 1.

The variation of dielectric constant ( $\epsilon$ ) and dielectric loss ( $\tan \delta$ ) with frequency for PMT ceramics measured at 323 K in the frequency range 100 Hz to 1 MHz is shown in figure 2. It is clear from figure 2 that all the samples showed dispersion in dielectric constant and dielectric loss at low frequency. The dielectric constant and dielectric loss initially showed a decrease with increase in frequency up to 10 kHz and then became more or less constant up to 1 MHz for PMT samples. The observations may be explained by the phenomenon of dipole relaxation. This is due to the inability of the electric dipoles to be in pace with the frequency of applied electric field. The low-frequency dielectric dispersion increased with the increase in Mn concentration and it was maximum for the  $x = 0.5$  sample. Figure 3 shows the magnetic susceptibility versus temperature plot for the  $\text{PbMn}_x\text{Ti}_{1-x}\text{O}_3$  system. The plots indicate that all the samples show a spontaneous magnetic moment, indicating a ferromagnetic nature. It is observed that on increasing the Mn concentration, the magnetization increases with a higher spontaneous moment and the ferromagnetic Curie temperatures ( $T_M$ ) are 613, 593 and 573 K

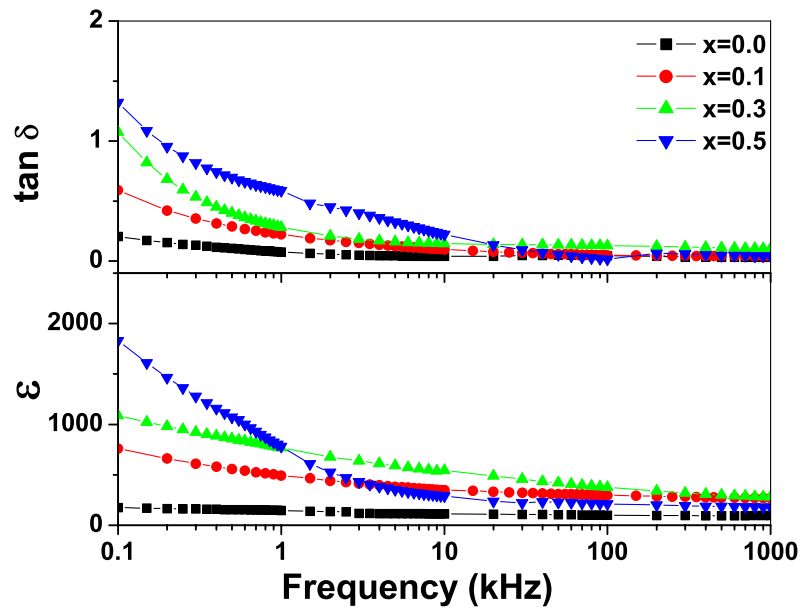


Figure 2. Frequency dependence of dielectric loss and dielectric constant of  $\text{PbMn}_x\text{Ti}_{1-x}\text{O}_3$  samples at 323 K.

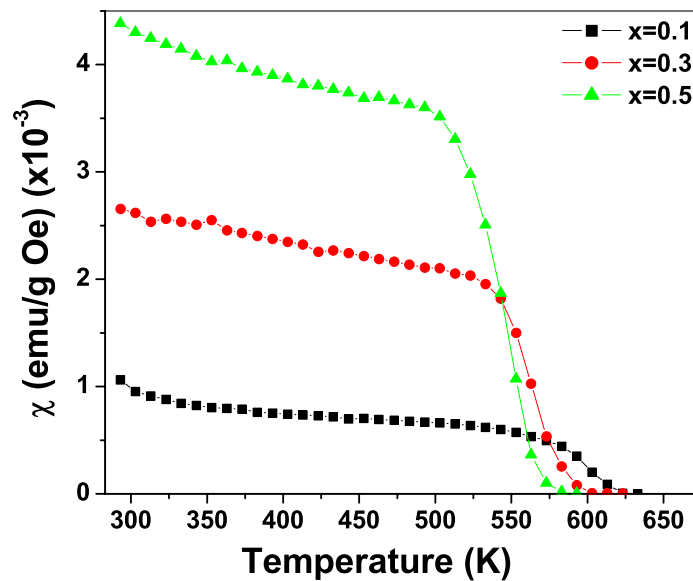
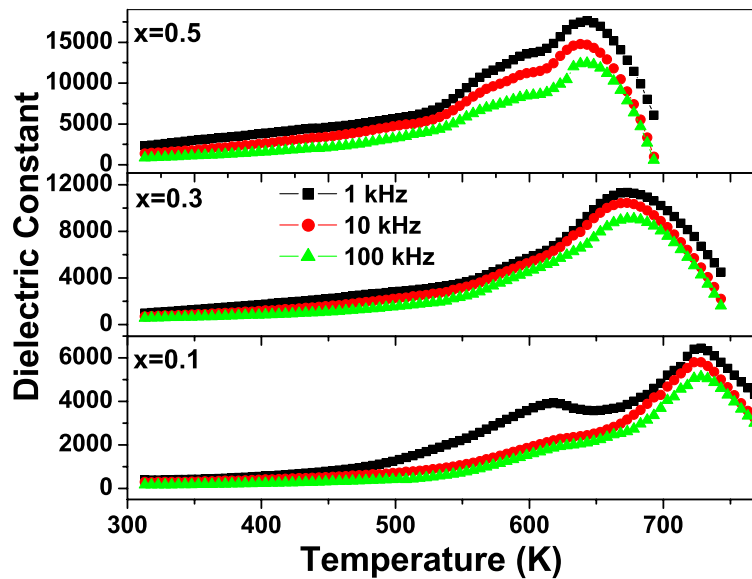


Figure 3. Variation of magnetic susceptibility with temperature for  $\text{PbMn}_x\text{Ti}_{1-x}\text{O}_3$  samples.

for  $x = 0.1, 0.3$  and  $0.5$ , respectively. The increase in magnetic moment on increasing the Mn content may be due to an increase in crystal ordering with the reduction in lattice distortion.

Dielectric measurements as a function of temperature carried out at different frequencies for PMT ceramics are shown in figure 4. Incidentally, a dielectric anomaly has been also observed in dielectric constant in the vicinity of ferromagnetic Curie temperature in all the



**Figure 4.** Variation of dielectric constant with temperature at frequencies 1, 10 and 100 kHz for  $\text{PbMn}_x\text{Ti}_{1-x}\text{O}_3$  samples.

samples. A small dielectric anomaly has been reported in the vicinity of the magnetic transition temperature in magnetoelectrically ordered systems as a consequence of vanishing magnetic order on electric order [6, 14]. Dielectric measurements showed broad peaks (diffuse type of phase transition) around 723 K (figure 4), which can be assigned to the ferroelectric phase transition for the  $x = 0.1$  sample. Similarly, peaks around 673 and 643 K can be assigned to the ferroelectric transition for  $x = 0.3$  and  $0.5$  samples, respectively. Pure  $\text{PbTiO}_3$  is known to have the ferroelectric Curie temperature ( $T_C$ ) at  $\sim 766$  K. On increasing Mn content in  $\text{PbMn}_x\text{Ti}_{1-x}\text{O}_3$  system, the ferroelectric phase transition temperature ( $T_C$ ) decreased as a consequence of reduction in lattice distortion.

Figure 5 shows the magnetization reversal curves for  $\text{PbMn}_x\text{Ti}_{1-x}\text{O}_3$  ceramics measured at 300 K using a SQUID magnetometer. Saturated magnetic reversal curves at 300 K revealed the ferromagnetic nature of  $\text{PbMn}_x\text{Ti}_{1-x}\text{O}_3$  ceramics consistent with the high-temperature magnetic susceptibility results. On increasing the Mn content in  $\text{PbMn}_x\text{Ti}_{1-x}\text{O}_3$  ceramics, the saturation magnetization increased and it was maximum for the  $x = 0.5$  sample. The ferroelectric loop measurement for the  $\text{PbMn}_{0.5}\text{Ti}_{0.5}\text{O}_3$  sample is shown in figure 6. Saturated ferroelectric hysteresis loops observed at room temperature indicate the presence of ferroelectricity. The magnetoelectric coupling in the  $\text{PbMn}_x\text{Ti}_{1-x}\text{O}_3$  system at room temperature was demonstrated by measuring the effect of magnetic field poling on the ferroelectric hysteresis loop. It was observed that after poling in a magnetic field at 1.2 T, the polarization increased about 11–13% for  $\text{PbMn}_x\text{Ti}_{1-x}\text{O}_3$  samples as compared to unpoled samples. In multiferroics, when a magnetic field is applied, the material will be strained. Due to the coupling between magnetic and ferroelectric domains, the strain will induce stress and then generate an electric field on the ferroelectric domain. As a result, the ferroelectric behaviour will be modified [6]. It is evidenced from figure 6 that an enhancement of  $\sim 13\%$  in saturation polarization was observed for  $\text{PbMn}_{0.5}\text{Ti}_{0.5}\text{O}_3$  sample. These results indicate the coupling between magnetic and ferroelectric order parameters in the  $\text{PbMn}_x\text{Ti}_{1-x}\text{O}_3$  system.

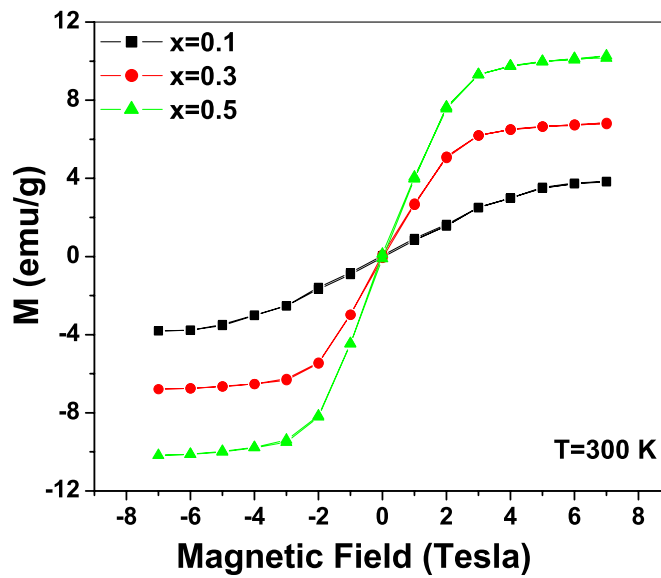


Figure 5. Magnetization versus magnetic field curves for  $\text{PbMn}_x\text{Ti}_{1-x}\text{O}_3$  samples at 300 K.

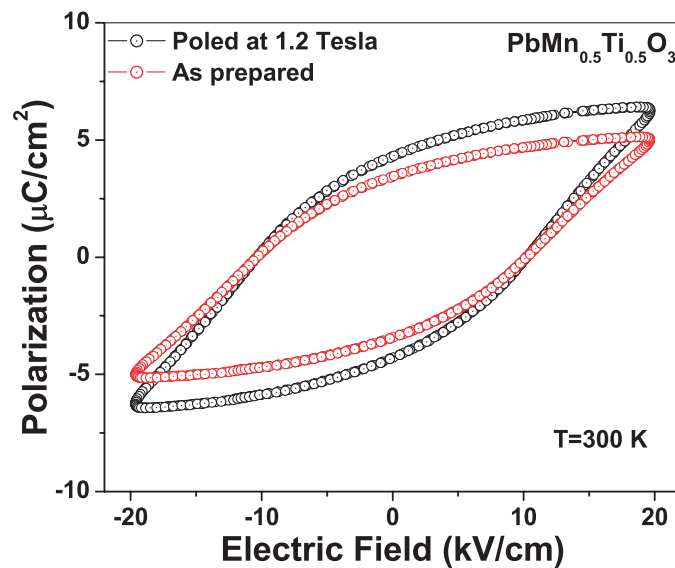


Figure 6. Electric field dependence of polarization of as-prepared and magnetic field poled  $\text{PbMn}_{0.5}\text{Ti}_{0.5}\text{O}_3$  samples at 300 K.

#### 4. Conclusion

We have studied the effect of Mn substitution in the  $\text{PbTiO}_3$  compound. Low-frequency dielectric dispersion was observed in the  $\text{PbMn}_x\text{Ti}_{1-x}\text{O}_3$  system. With increasing Mn substitution, the lattice distortion reduced, which in turn decreased the ferroelectric Curie temperature ( $T_C$ ). The ferromagnetic Curie temperatures ( $T_M$ ) were found to be 613, 593 and 573 K for  $x = 0.1, 0.3$  and  $0.5$  samples, respectively. An anomaly was observed in the dielectric

constant near the ferromagnetic Curie temperature. The results of magnetic and ferroelectric measurements point to the coupling between magnetic dipoles and electric dipoles at room temperature in the  $\text{PbMn}_x\text{Ti}_{1-x}\text{O}_3$  system. It is significant that the coexistence of magnetic and electric ordering at room temperature in the  $\text{PbMn}_x\text{Ti}_{1-x}\text{O}_3$  system and the decrease in the magnetic and ferroelectric Curie temperature towards room temperature make it a potential candidate for device applications.

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