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# Effect of manganese on thermal, structural and magnetic properties of lanthanum modified lead titanate nanoceramics

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ABSTRACT

$PbTiO_3$ (PT) and La/Mn modified $PbTiO_3$ (PLMT) nanoceramics were prepared by mechanical alloying and thermal methods. A thermal analysis technique has provided some important clues and guidelines for formation of required compounds and their thermal stability. The formation of single-phase perovskite compounds was confirmed by an X-ray diffraction technique. The field emission scanning electron micrograph of the compounds shows that materials have well-defined granular morphology. La/Mn substitution at Pb/Ti sites reduces the lattice distortion, and decreases ferroelectric phase temperature of lead titanate. Room temperature *P–E* loop confirms the existence of ferroelectric ordering in the sample. The nonlinear *M–H* hysteresis loop with small magnetization revealed that a ferromagnetic property is observed in $PbTiO_3$ due to the substitution of Mn at Ti-sites of $PbTiO_3$

## 1. Introduction

In the past few years, there has been significant enhancement in the performance and applications of multiferroic materials. Multiferroic materials, which display coexistence of ferromagnetism and ferroelectric polarization, have received increased attention because of their interesting and potential properties for multifunctional devices [1].

Unfortunately, multiferroic materials are very rare due to exclusiveness of partially filled atomic orbitals (for magnetic dipoles or moments) and the occurrence of local electric dipoles, which are typically associated with the presence of either empty d-shells and/or an electron lone-pair configuration [2]. Despite this apparently bad compatibility of magnetism and ferroelectricity, researchers have discovered plenty of systems in which these properties coexist, and many more to come in near future.

The structural classification of multiferroic materials includes perovskies, layered perovskites magnetic boracites, hexagonal manganites, rare earth doped manganites, etc. In 1980, Ismailzade et al. [3] reported the presence of linear ME effect in $BiFeO_3$, a perovskite structured compound of antiferromagnetic–ferroelectric nature. Its combination with bismuth titanate and barium titanate leads to a family with Aurrivilius structure and shows the coexistence of ferroelectric and ferromagnetic nature up to high temperatures [4]. Spontaneous magnetization in BFO can be induced by the substitution of $Fe^{3+}$ by other transition metal ions [5]. Again B-site ions substitution decreases magnetic ordering temperature drastically [6], thus hampering their application at room temperature. Schmid [7] has worked on boracites belonging to the large crystal structure family with a general formula $M_3B_7O_{13}X$, where M stands for a bivalent cation of $Mn^{2+}$, $Fe^{2+}$, $Co^{2+}$, $Ni^{2+}$, $Cu^{2+}$, $Zn^{2+}$, etc. and X stands for a monovalent anion like $OH^-$, $F^-$, $Cl^-$, $Br^-$, $I^-$ or $NO^{3-}$.

Typical multiferroics belong to the group of perovskite transition metal oxides. The design and development of perovskites transition-metal oxides have attracted much interest because of their wide variety of physical properties (ferroelectricity, magnetism and superconductivity), originating from lattices, spin and orbital couplings [8]. In the perovskite titanate oxides (i.e., $PbTiO_3$, $BaTiO_3$, etc.) 3d transition metals can be simply substituted at the titanium site due to their close resemblance to the titanium ion in size and valency [9]. The search on the ferromagnetism–ferroelectricity phenomenon in the same material began in Russia in the 1950s, with the replacement of some $d^0$ B cations in ferroelectric perovskite oxides by magnetic $d^n$ cations [10]. Kumar and Yadav [11] reported the conversion of enhanced multiferroic properties in $Pb_{(1-x)}Ba_x(Fe_{0.5}Ti_{0.5})O_3$.

Though some works on multiferroic properties of Mn-substituted PT are available [12] in the literature, detailed studies of dielectric and magnetic properties (with low concentration) of La/Mn modified

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$PbTiO_3$ nanoceramics have not been reported so far. Therefore, we have extensively studied these properties and reported them in this paper.

## 2. Experimental details

The polycrystalline samples of pure $PbTiO_3$(PT) and $Pb_{0.88}La_{0.12}(Ti_{0.90}Mn_{0.10})_{0.97}O_3$ (PLMT) were prepared by mechanical alloying and thermal methods. The milling was carried out in a Fritsch Pulverisette P5 planetary ball mill at room temperature for 50 h. A thermal gravimetric analyzer (Perkin-Elmer thermal analyzer (model: diamond)) (TGA) was used to check the phase formation temperature of the samples. Then the powders were calcined at optimized temperature (400 °C) and time (6 h). X-ray diffraction data were collected by a Rigaku Miniflex with CuKα radiation ($\lambda=1.5418$ Å) at scanning rate of 2°/min. Sintering was performed at 1000 °C for 2 h in a sealed alumina crucible. The sintered pellets were electroded with silver paint on their flat faces prior to dielectric measurements. Dielectric and related parameters were obtained using a computer-controlled impedance analyzer (HIOKI LCR Hi TESTER, Model: 3532) in conjunction with a laboratory-made sample holder in the frequency range from 100 to 1 MHz at different temperatures (from RT to 500 °C). The polarization measurement (hysteresis loop) of a poled PLMT (5.2 kV/cm) sample was carried out using a workstation of hysteresis loop tracer (M/S Radiant Technology, Inc., USA). The magnetic measurement was carried out using an Ever Cool Superconducting Quantum Interference Device (SQUID) VSM DC magnetometer (Quantum Design, USA).

## 3. Results and discussion

### 3.1. Thermal and structural analyses

Fig. 1 shows TG plots of pure PT (inset) and PLMT compounds. Thermal gravimetric (TG) curves show water removal at 120 °C followed by the second weight loss at 200 °C which can be attributed to the decomposition of species originating from the milling process [13]. The low calcination temperature supports the expected advantage of high-energy ball milling as compared to the solid-state reaction counterpart [14].

Fig. 2 shows the room temperature X-ray diffraction (XRD) pattern of pure PT and PLMT samples. All XRD peaks were indexed using a standard computer program POWDMULT [15]. Preliminary structural analysis suggests tetragonal structure of the materials. At room temperature, lattice constants of pure PT are $a=3.899$ Å Q2 and $c=4.154$ Å [16]. The least-square refined unit cell parameters of PLMT are $a=3.9373$ Å and $c=$ 4.0792 Å. The average crystallite size and lattice strain of the PLMT samples carried out using X'Pert HighScore software [17] were found to be 34 nm, 30 nm and 0.275, 0.289 respectively.

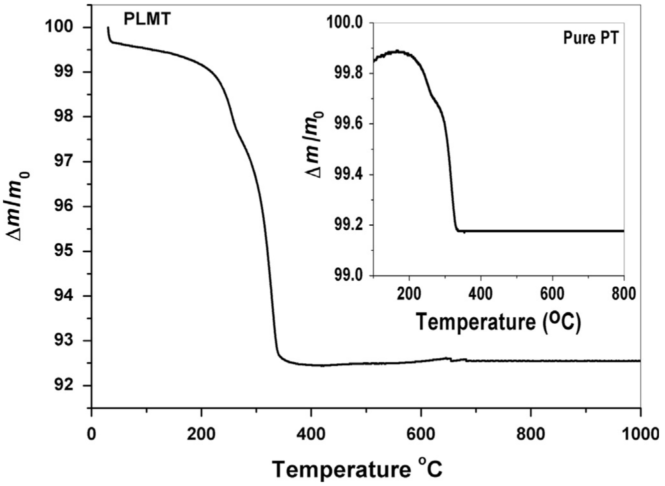

**Fig. 1.** TG pattern of pure PT (inset) and PLMT compounds.

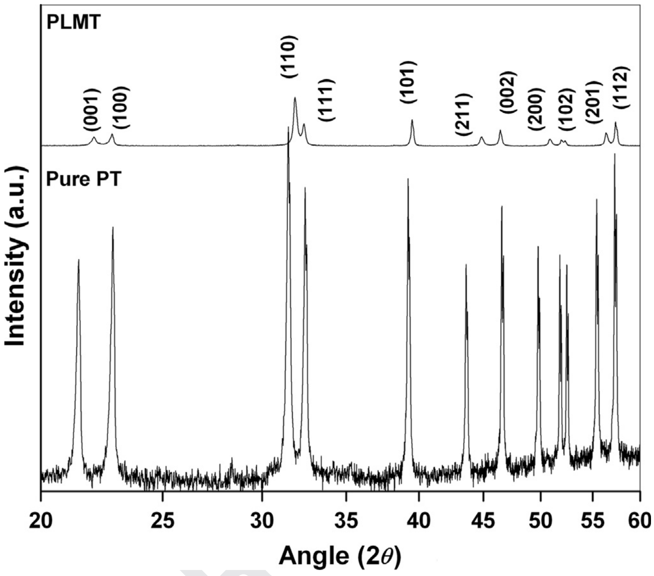

**Fig. 2.** XRD pattern of pure PT and PLMT compounds.

### 3.2. Microstructural analysis

Fig. 3 shows field emission scanning electron micrographs (FESEM) of pure PT and PLMT compounds. The micrographs show polycrystalline nature of all micrographs. The grains of nearly equal size and shape are distributed homogeneously throughout the surface of the samples required for applications [18]. A highly dense microstructure is obtained with a decrease in grain size on incorporation of La/Mn content. Being an acceptor ion, $Mn^{4+}$ may replace $Ti^{4+}$ sites, and as an additive segregate at grain boundaries which can prevent grain growth [19].

### 3.3. Dielectric study

Fig. 4 shows the temperature dependence of the dielectric permittivity for pure PT (inset) and PLMT compounds. The Curie temperature of pure $PbTiO_3$ is 490 °C and its value is lowered on addition of La/Mn in PT. As can be seen, no evidence of relaxor like dielectric response was observed for PLMT with the increase of frequency. The transition temperature shifts towards lower temperature side (260 °C) with lanthanum substitution in PT. This can be attributed to the decrease in crystal tetragonality caused by La substitution, which reduces the internal stress, which in turn, reduces transition temperature [20]. Since the manganese ion is substituted for $Ti^{4+}$ ions at B-sites of the perovskite structure, upon manganese substitution an important effect on phase transition temperature is not expected [21].

### 3.4. Polarization study

Hysteresis loop of poled PLMT sample at room temperature (50 Hz) has been given in Fig. 5. The poling of pure and dense lead titnate ceramic is very difficult because of its fragile and porous nature. Due to high conductivity, the measurement of *P–E* loop for Mn based materials has also been difficult [22]. Thus saturation

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