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Ferroelectric phase-transition and conductivity analysis of La^{3+}/Mn^{4+} modified $PbTiO_3$ nanoceramics

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ABSTRACT

The nanocrystalline samples of $Pb_{0.92}La_{0.08}Mn_xTi_{1-x}O_3$ (PLMT) ($x=0.00$, 0.04, 0.07, 0.10) were prepared by using a novel mechanical activation followed by a conventional solid-state reaction technique. The calcination and sintering temperatures were optimized by thermal gravimetric analysis and repeated firing. Preliminary structural studies using high resolution X-ray diffraction (HRXRD) technique at room temperature suggest that compounds are formed in a single phase with tetragonal crystal system. The field emission scanning electron microscopy (FESEM) shows that materials have well-defined granular microstructures, separated by the grain boundaries. The high resolution transmission electron microscopy (HRTEM) confirms about the nano-size of the particles. The ferroelectric phase-transition of PLMT materials is studied using dielectric measurements, which shows a shift in the transition temperature towards the lower-temperature side with increased doping concentration. The electrical conductivity calculated from impedance data has been observed to increase as a function of Mn concentration. The ac conductivity spectrum analysis suggests hopping of charge carriers among localized site as the possible mechanism for electrical conduction. The activation energy of the materials was found sensitive to its crystallite size.

1. Introduction

Perovskite-type (ABO_3) oxides have gained much attention as having many excellent physical properties such as ferroelectric, piezoelectric, magnetoelectric and electrooptic effects [1–4]. Among the perovskite-type oxides, titanate-ceramics have been considered as interesting materials for room temperature applications mainly due to their high dielectric properties. Lead titanate ($PbTiO_3$), which exhibits a perovskites structure and a very high Curie temperature of 490 °C, belongs to the most important ferroelectric and piezoelectric families [5]. The phase transition behaviour in a $PbTiO_3$ single crystal is relatively simple; it exhibits a single transition from paraelectric Curie phase to ferroelectric tetragonal phase [6]. The substitution of any suitable ions at the Pb and/or Ti site of lead titanate causes a lowering of Curie temperature [7]. Beside it, doping has also been proved to be an effective way in controlling the ferroelectric behaviour of lead titanate. The doping subsistent can either occupy A-site, B-site or both as donor or acceptor based on chemical valance with respect to the original ions [8]. Manganese (Mn^{+4}) as an acceptor ion may replace Ti^{+4} site and as addition segregates at grain boundaries [9]. Mn doping in lead titanate is also good candidate for fabricating piezoelectric devices [10]. Mn belongs to valence unstable ions; it can affect the stability of material. The introduction of an optimized amount of lanthanum (La) not only increases the stability but also softens the ferroelectric properties of material. It also enhances the dielectric property and remanent polarization, as well as reduces the coercive field which is favoured in ferroelectric random access memory (FERAM) applications [8]. It is also well known that the fluctuation of the oxidation state of the transition metal ions (Fe^{3+}, Mn^{3+}) results in the formation of oxygen ion vacancies to reserve the local electrical neutrality and causes thermally activated conduction [11]. The oxygen vacancy concentration in rare earth (La) and manganese modified lead titanate could have an important contribution to the electrical response of these materials, i.e. the dielectric relaxation processes and also the electrical conductivity behaviour. Considering all these features we have characterized La^{+3}/Mn^{+4} modified lead titanate with a general formula $Pb_{0.92}La_{0.08}Mn_xTi_{1-x}O_3$ ($x=0.0$, 0.04, 0.07, 0.10), which is prepared by using high energy ball milling followed by some heat treatment. This technique provides many advantages over conventional solid-state reaction method [12]. In this technique formation at high strain rates leads to the fabrication of nanoparticles. Nanocrystalline materials are found to superior over the polycrystalline coarse-grained materials [13].

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2. Experimental details

Lanthanum (La^{+3}) and manganese (Mn^{+4}) modified lead titanate (PLMT) nanoceramics with a general formula $Pb_{0.92}La_{0.08}Mn_xTi_{1-x}O_3$ ($x=0.0$ 0.04, 0.07, 0.10) were synthesized from high purity ($\geq 99.9\%$) oxides; PbO (with 5 wt% excess) (M/s B.D.H Chemicals), La_2O_3 (M/s Loba Chemie. co. India), TiO_2 (M/s S.D. fine Chemicals Ltd.) and MnO_2 (M/s Loba Chemie.co.India) by a high-energy ball-milling technique followed by a solid-state reaction method. The milling was carried out in a Fritsch Pulverisette P5 planetary ball mill at room temperature for different milling times (10, 20, 30, 40 and 50 h). Milling was carried out in toluene medium (toluene is chemically inert and can be used to diffuse heat that is generated during milling) with WC (tungsten carbide) and milling media at a speed of 300 rpm and a ball to powder weight ratio of 10:1, the milling stopped for 30 min after every 1 h of milling to cool down the system. The air-dried powders were heat-treated using thermal gravimetric analyzer (Perkin-Elmer thermal analyzer (model: diamond)) (TGA) to obtain the calcination temperature (at a heating rate of 10 °C/min in argon atmosphere from room temperature up to 1200 °C). Then the powders were calcined at optimized temperature (600 °C) and time (6 h) (based on thermal analyzer and repeated calcinations process) in a programmable furnace with an accuracy of ± 1 °C. The formation of single phase compounds was confirmed by highly resolution X-ray diffraction data collected by PANalytical high resolution XRD-I, PW 3040/60 with CuKα radiation ($\lambda=1.5418$ Å) in a wide range of Bragg's angles 2θ ($20^\circ \leq 2\theta \leq 80^\circ$) with scanning rate of 4 °/min. The high resolution transmission electron micrographs (HRTEM) of the calcined powders were taken by JEOL, JSM (Model-2100) in order to obtain the shape and size of the particles. The powder samples were dispersed in acetone through sonication and then placed on a carbon-coated grid with a mesh size of 200. The calcined powders were used to make cylindrical pellets of diameter 5 mm and thickness 1–2 mm using a hydraulic press at a pressure of 6×10^7 N/m^2. Polyvinyl alcohol (PVC) was used as a binder to prepare the pellets. These pellets were sintered at the optimized temperature (1000 °C) for 10 h in an air atmosphere. The field effect scanning electron micrographs and energy dispersive X-ray analysis (EDAX) are recorded (CARL ZEISS SUPRA 40) to study the surface morphology/microstructure and chemical composition of the PLMT sintered pellets. The pellet samples were gold coated prior to being scanned under high-resolution field emission gun of FESEM. The gold coating was carried out under argon (Ar) atmosphere. In order to study the electrical properties, both flat surfaces of the samples were polished and electroded with high purity silver paint, and then dried at 150 °C in oven for 3 to 4 h to remove moistures. The electrical measurements were carried out at an input signal level of 1.5 V in a wide temperature range (35–500 °C) using a computer-controlled impedance analyzer, HIOKI LCR meter, (Model: 3532) in the frequency range of 1 kHz to 1 MHz. The pellets were sintered at 1000 °C for 2 h in an air atmosphere. The measured density of the sintered PLMT pellets was found to be within 97–98% of its theoretical density.

3. Results and discussions

3.1. Thermal analysis

Fig. 1 shows the TGA graph of $Pb_{0.92}La_{0.08}Mn_xTi_{1-x}O_3$ ($x=0.0$, 0.04, 0.07, 0.10). The graphs demonstrate a two-stage weight loss for comparison of the compounds. It is observed that the mass loss ($\Delta m/m_o$) attains a saturated value almost at 578 °C for all the compounds. The weight loss up to 130 °C may be associated to the departure of water molecules during thermal decomposition of the precursors. The progressive mass loss up to 578 °C, could be assigned to the lead loss at high temperature. So it is clear from the curve that the precursor materials should be heated well at 600 °C temperature.

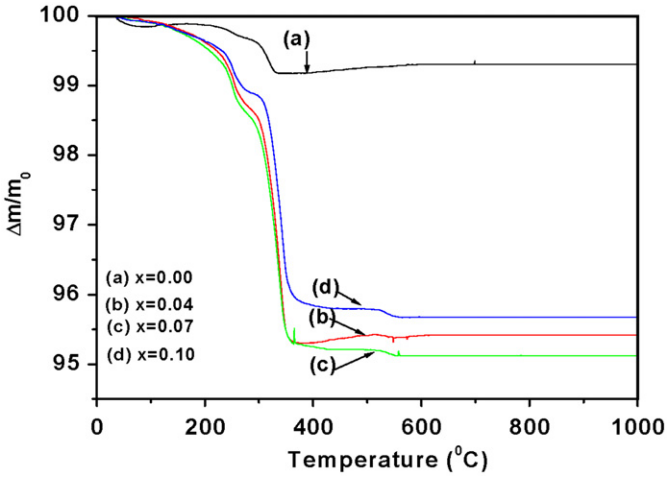

Fig. 1. TGA pattern of PLMT ($x=0.0$, 0.04, 0.07, 0.10) compounds.

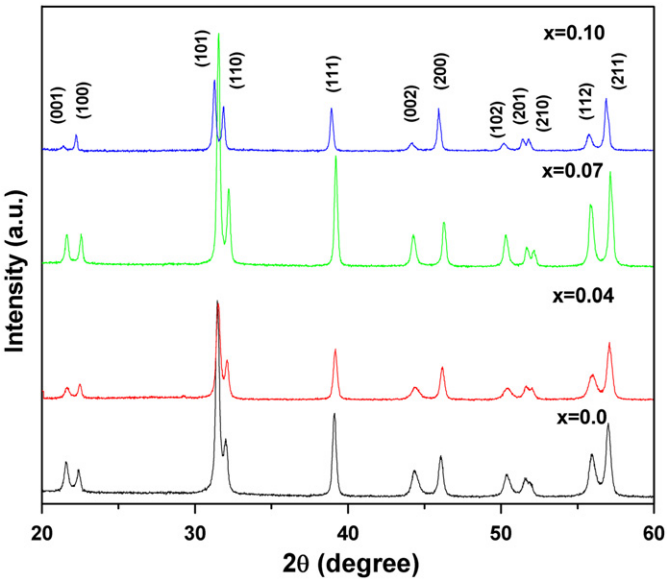

Fig. 2. Room temperature HRXRD pattern of PLMT ($x=0.0$, 0.04, 0.07, 0.10) compounds.

3.2. Structural characterization

Fig. 2 shows the high resolution X-ray diffraction (HRXRD) patterns of $Pb_{0.92}La_{0.08}Mn_xTi_{1-x}O_3$ ($x=0.0$, 0.04, 0.07, 0.10). Lead titanate is a displacive type of ferroelectric compound having tetragonal structure with very large lattice distortion from a cubic structure [14]. All the peaks of the HRXRD pattern of the PLMT ceramics were indexed and the lattice parameters were determined in various crystal systems using a computer program "POWDMULT" [15]. The best agreement between observed (obs) and calculated (cal) interplanar spacing d (i.e., $\Sigma d_{obs}-\Sigma d_{cal}=$minimum) was found in the tetragonal crystal system like that of the parent compound. Since the ionic radius of Mn^{4+} is smaller than that of Ti^{4+}, the tetragonal ratio (c/a) and