Available online at www.sciencedirect.com

SciVerse ScienceDirect

Ceramics International 38 (2012) 1549–1556

CERAMICS INTERNATIONAL

www.elsevier.com/locate/ceramint

Structural investigation and dielectric studies on Mn substituted $Pb(Zr_{0.65}Ti_{0.35})O_3$ perovskite ceramics

Niranjan Sahu [a], S. Panigrahi [a], Manoranjan Kar [b,*]

[a] Department of Physics, National Institute of Technology, Rourkela 769008, Odisha, India
[b] Department of Physics, Indian Institute of Technology Patna, Patna 800013, Bihar, India

Received 30 January 2011; received in revised form 21 September 2011; accepted 21 September 2011
Available online 28 September 2011

Abstract

Polycrystalline samples of manganese substituted lead zirconium titanate (PZMT) with general formula $Pb(Zr_{0.65-x}Mn_xTi_{0.35})O_3$ ceramics have been synthesised by high temperature solid state reaction technique. X-ray diffraction (XRD) patterns were recorded at room temperature to study the crystal structure employing Rietveld technique. All the patterns could be refined to *R3c* space group with rhombohedral symmetry. Bond lengths and angles have been calculated from refined parameters. Microstructural properties of the materials were analysed by scanning electron microscope (SEM) and compositional analysis were carried out by energy dispersive spectrum (EDS) measurements. All the materials exhibit ferroelectric to paraelectric transition. The Curie temperature (T_c) increases with the Mn concentration. We have observed that dielectric constant decreases and AC conductivity increases with the frequency. The correlation between lattice parameters and T_c for the present samples has been observed.

Keywords: Rietveld; Dielectric; PZT; XRD; Perovskite

1. Introduction

Lead zirconate titanate (PZT) with chemical formulae $Pb(Zr_{1-x}Ti_x)O_3$ is a family of ferroelectric compound which have been studied in detail due to their interesting physical and technological properties [1–3]. However, the structure of PZT is the point of discussion till today. For many years, the crystal structure of PZT was thought to be as indicated by the well known phase diagram published by Jaffe et al. [4]. The morphotropic phase boundary (MPB) region mostly defined in the range $0.4 < x < 0.6$. Most of the research interest has been devoted in this region, because of the extremely high piezoelectric response which has numerous technological applications [5–7]. Depending upon the specific requirement of piezoelectric ceramics, suitable compositions of the PZT system may be chosen [8]. Further, various substituents are added in the PZT system and the properties have been tailored to meet requirements for desired applications [9–11]. However, there are a few reports on substituting transition element either in Zr site or Ti site of the composition Zr/Ti = 65/35 which is beyond the MPB [12,13]. In this composition, several groups have shown the better physical properties which can be transformed for industrial applications [9,10]. In last few years, Mn element has attracted researchers for substitution in Zr site of PZT perovskite due to its comparable ionic radius and magnetic nature which leads to design a new multiferroic material [14–17]. There are a few reports on Mn doped in Zr site of PZT material [18–24]. Hysteretic properties of Mn-doped $Pb(Zr_{0.30}Ti_{0.70})O_3$ thin films has been studied by Zhang and Whatmore [19]. Coercive field increases with the Mn concentration in PZT thin films. Tiwari et al. [20,21] have studied structural and dielectric properties of $Pb(Zr_{0.65-x}Mn_xTi_{0.35})O_3$ ceramics. They have prepared the sample by annealing at 900 °C. The grain sizes of their samples are close to 1 μm. They have observed that, the curie temperature (T_c) increases for $x = 0.05$ and then decreases with the Mn concentration.

The effect of Mn modification on PZT(65/35) ceramics shows the improvement of dielectric constant, Curie temperature and dielectric loss. However, there are inadequate reports on correlation between crystal structure and physical properties on Mn doped PZT materials. Hence, detailed study on crystal structure and electrical properties is required to understand the correlation between them.

* Corresponding author. Tel.: +91 61 22552013; fax: +91 61 22277383.
E-mail address: mano@iitp.ac.in (M. Kar).

0272-8842/$36.00
doi:10.1016/j.ceramint.2011.09.040

In the present study we have doped Mn ions in place of Zr in PZT. The detailed crystal structure has been studied by employing Rietveld analysis. The correlation between crystal structure and dielectric properties has been observed. We have observed that, the T_c and maximum dielectric constant increases with the decrease of lattice parameters and bond lengths. The dielectric constant suggests that, the present material can be a potential element for manufacturing multilayer ceramic capacitors.

2. Experimental technique

Perovskite $Pb(Zr_{0.65-x}Mn_xTi_{0.35})O_3$ (Zr/Ti = 65/35) with $x = 0.00$, 0.05, 0.10 and 0.15 ceramics have been prepared by high temperature solid state reaction technique. Stoichiometric ratio of PbO (Loba Chem., Mumbai), ZrO_2 (Loba Chem., Mumbai), MnO_2 (E. Merck India Ltd.), and TiO_2 (E. Merck India Ltd.) with 99.9% purity was weighed by using a high precision electronic balance. The above materials were mixed thoroughly with the help of agate mortar and pestle. The grinding was carried out under acetone till the acetone evaporates from the mortar. The mixture was ball milled for 8 h and presintered at different temperatures with intermediate grindings. Finally the powder was calcined at 900 °C for 8 h. The fine powders of the above compounds were pressed into cylindrical pellets of 6 mm diameter and 1 mm thickness under a uni-axial pressure of 6 ton using a hydraulic press. Polyvinyl alcohol (PVA) was used as the binder to make pellets. Finally the pellets were sintered at 1100 °C for over 4 h in a alumina crucible and 5% extra lead oxide was added to prevent lead loss at high temperature and then cooled to room temperature at the rate of 2 °C min^{-1}. All the above sintering processes were carried out in air. The bulk densities of the sintered samples were measured by the Archimedes principle using distilled water as medium and found to be 97–98% of the theoretical density. XRD pattern at room temperature for the sample was recorded by using Philips PANalytical X'pert – MPD X-ray diffractometer (XRD) (Model-PW3020). The CuKα radiation was used as X-ray source. The machine was operated at 35 kV and 30 mA in a wide range of Bragg angles 2θ ($20^\circ \leq 2\theta \leq 80^\circ$). The data was collected with step size of 0.020° and time constant of 1 s. The scanning electron micrograph was recorded using JEOL SEM (JEOL T-330) at room temperature. The compositional analysis was carried out by SEM-EDS.

The dielectric (capacitance and dissipation) and impedance parameters were obtained at an input signal level of 1.3 V in a wide temperature range of 40–500 °C and frequency range of 100 Hz–100 kHz using a computer-controlled LCR HiTESTER/Impedance analyser (HIOKI 3522-50). The temperature variation was obtained by a high temperature furnace (Model: DPI-1200).

We have calculated the average crystallite size by using Scherrer's formulae, Williamson–Hall, and Rietveld method. The Scherrer's formulae can be written as [25],

$$S_C = \frac{\kappa\lambda}{\beta\cos\theta} \quad (1)$$

where constant 'k' depends upon the shape of the crystallite size (0.89, assuming the circular grain), β, Full Width at Half Maximum (FWHM) of intensity vs. 2θ profile, λ is wavelength of the CuKα radiation (0.15418 nm) and θ is the Bragg's diffraction angle. The instrumental broadening factor has been taken into account during the FWHM calculation ($\beta = \sqrt{\beta_{obs}^2 - \beta_{ins}^2}$).

According to Williamson–Hall (WH) method [26], the individual contributions to the broadening of reflections can be expressed as

$$\beta\cos\theta = \frac{k\lambda}{S_C} + 4e\sin\theta \quad (2)$$

where $4e\sin\theta$ is the strain effect on the crystallites. It is mostly the correction of Scherrer's formula by taking into account of strain. The 2θ range of 20° to 80° were used to construct a linear plot of $\beta\cos\theta$ versus $\sin\theta$ (figure not shown), from which the average crystallite size and the strain were obtained using Eq. (2).

A complete expression is used in Rietveld method which can be written as [27,28],

$$FWHM^2 = (U + D_{ST}^2)(\tan^2\theta) + V(\tan\theta) + W + \frac{IG}{\cos^2\theta} \quad (3)$$

where U, V and W are the usual peak shape parameters, IG is a measure of the isotropic size effect, D_{ST} coefficient related to strain. IG and D_{ST} can be refined in Rietveld method.

3. Results and discussions

3.1. Structural and morphology

XRD patterns (not shown) of $Pb(Zr_{0.65-x}Mn_xTi_{0.35})O_3$ for $x = 0.00$, 0.05, 0.10 and 0.15 samples annealed at 800 °C reveal that, the samples are in mixed phase. Hence, these samples were annealed at 900 °C and 1100 °C and, XRD patterns for all the samples are shown in Figs. 1 and 2 respectively. We have observed that the samples are almost in single phase form. All the observed peaks could be indexed using *R3c* space group with rhombohedral symmetry except some minor peaks at 26°, 28° and 34°. These small peaks could be due to growth of tetragonal phase of PZT as the parent composition is very close to the MPB region. However, we have not considered those peaks in our analysis as they are very small.

The XRD patterns for all the samples were analysed with the help of Fullprof program by employing Rietveld refinement technique [27,28]. Typical refined XRD pattern of $Pb(Zr_{0.60}Mn_{0.05}Ti_{0.35})O_3$ sample (annealed at 1100°C) is shown in Fig. 3. We have observed that all the peaks could be well refined to *R3c* spacegroup. Lattice parameters, occupancy, fractional atomic positions, etc. were taken as the free parameter during the fitting. The lattice parameters, goodness of the fitting are listed in Table 2. The fractional atomic positions are Pb (0, 0, 0.29030), Zr/Ti (0, 0, 0.01776) and O (0.25963, 0.44976, 0.10665) for $x = 0.00$ (*R3c*) sample. The refined lattice parameters are listed in Table 2. These values are comparable to those of the literature reported values