Ceramics International 42 (2016) 14490–14498

Contents lists available at ScienceDirect

Ceramics International

journal homepage: www.elsevier.com/locate/ceramint

Spherical ferroelectric $PbZr_{0.52}Ti_{0.48}O_3$ nanoparticles with high permittivity: Switchable dielectric phase transition with temperature

Suryakanta Nayak [a,b,*], Tapan Kumar Chaki [b], Dipak Khastgir [b,**]

[a] Department of Mechanical Engineering, National University of Singapore, Kent Ridge, Singapore 117576, Singapore
[b] Rubber Technology Centre, Indian Institute of Technology Kharagpur, West Bengal 721302, India

ARTICLE INFO

Article history:
Received 11 May 2016
Received in revised form
8 June 2016
Accepted 8 June 2016
Available online 9 June 2016

Keywords:
Permittivity
Ceramic
Nanoparticle
Electric modulus
Temperature

ABSTRACT

The spherical ferroelectric $PbZr_{0.52}Ti_{0.48}O_3$ (PZT 52/48) nanoparticles are prepared *via* simple and environment friendly high temperature solid state method. The crystal structure and morphology of these particles are characterized by X-ray diffraction (XRD), high resolution transmission electron microscopy (HRTEM), and field emission scanning electron microscopy (FESEM). XRD analysis and selected area electron diffraction (SAED) pattern of PZT particles revealed its crystalline nature. The energy involved in the synthesis especially during the initiation and termination processes for the formation of PZT particles is found from the high temperature calorimetric study. These particles are spherical in nature with an average diameter of ≤ 20 nm. The bulk and surface chemical composition of these particles are investigated by Fourier transform infrared (FTIR) spectroscopy and X-ray photoelectron spectroscopy (XPS). XPS study reveals that the prepared PZT particles contain titanium ion in two different oxidation states namely Ti^{3+} and Ti^{4+}. The PZT particles exhibit high permittivity with relatively low dielectric loss. From temperature dependent dielectric analysis, it is seen that there is a switchable dielectric phase transition at or above 80 °C.

1. Introduction

Ferroelectric perovskite materials exhibiting high dielectric constant and piezoelectric coefficient have attracted the attention of many material researchers over the past decades [1]. Piezoelectricity is the ability of certain crystalline materials to develop an electric charge proportional to a mechanical stress which was discovered by J. and P. Curie in 1880 [2]. Lead based titanates exhibit remarkable piezoelectric, pyroelectric, and optoelectronic properties and are very important for the electronic devices [3]. Lead zirconium titanate, $PbZr_{0.52}Ti_{0.48}O_3$ (PZT 52/48) particles are ferroelectric in nature which shows spontaneous polarization by the application of external electric field and extensively used in piezoelectric applications [2,4–6]. Since 1950 s, the pioneering work of Shirane and co-workers, the lead zirconate titanate $PbZr_{1-x}Ti_xO_3$ (PZT) system has been considered in number of studies such as actuators and nonvolatile memory applications [7]. PZT particles also show good piezoelectric behavior which makes them suitable for application in microelectromechanical systems (MEMS) [8]. These particles have other various applications such as microelectronic devices, infrared detectors, high energy capacitors, ultrasonic sensors, accelerometers, and non-volatile memories etc. [6,9].

PZT has a distorted perovskite structure below 350 °C with a ferroelectric tetragonal or rhombohedral phase and consequently shows a spontaneous polarization [10]. The exceptional piezoelectric properties of $PbZr_{1-x}Ti_xO_3$ ceramic have been attributed to a mixture of ferroelectric tetragonal (F_T) and rhombohedral (F_R) phases for compositions ($x \approx 0.48$), which is known as morphotropic phase boundary (MPB) [11]. Moreover, a second monoclinic phase with a doubled unit cell has been observed at low temperatures for $PbZr_{0.52}Ti_{0.48}O_3$ [12,13]. It has been observed that a monoclinic phase (F_M) is present in between F_R and F_T where F_M serves as a transition between the above two phases at temperatures below 300 K. In the monoclinic phase (F_M), the direction of polarization can lie anywhere between [111] and [001] directions which provides high piezoelectric response [1,11,14].

The polarization direction of PZT crystal changes between two stable polarization states corresponding to the positive and negative electric bias. This feature makes PZT a good candidate for nonvolatile ferroelectric random-access memories (NFERAM) [10,15]. In order to prepare PZT ceramic of good properties, it should have narrow MPB and stoichiometrical homogeneous composition, which require the PZT powder of good thermal

* Corresponding author at: Department of Mechanical Engineering, National University of Singapore, Kent Ridge, Singapore 117576, Singapore.
** Corresponding author.
E-mail addresses: suryakanta.iitkgp@gmail.com (S. Nayak), khasdi@rtc.iitkgp.ernet.in (D. Khastgir).

http://dx.doi.org/10.1016/j.ceramint.2016.06.056
0272-8842/

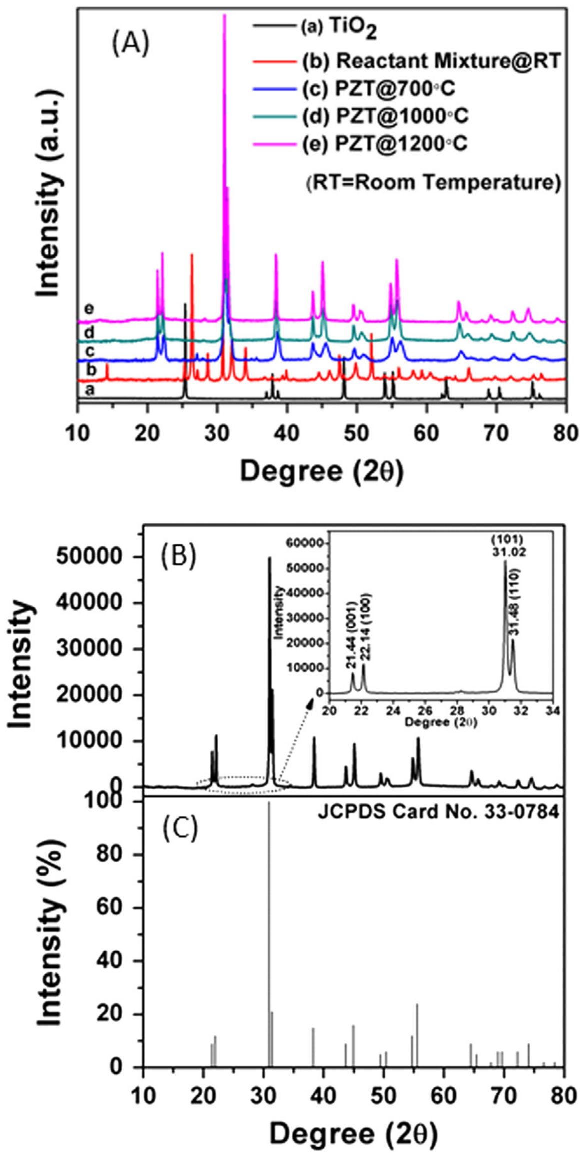

Fig. 1. XRD pattern of (A) TiO_2, reactant mixtures, and PZT particles at different reaction conditions; (B) prepared PZT particles at 1200 °C; and (C) plot obtained from the JCPDS analysis for $PbZr_{0.52}Ti_{0.48}O_3$ particles.

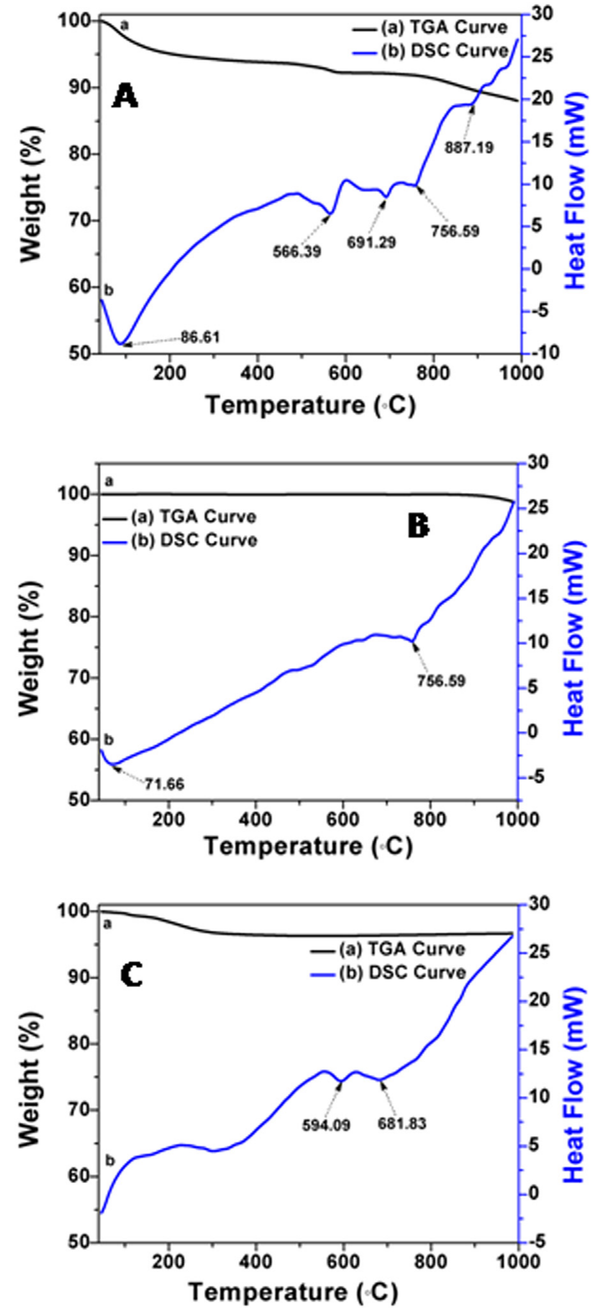

Fig. 2. TGA/DSC curve for mixture of TiO_2, $Zr(OH)_2$, and Pb_3O_4 (A) 1st run, (B) 2nd run; TGA/DSC curve of (C) prepared PZT particles through solid state reaction.

stability and high sintering activity [16]. Xu et al. have prepared PZT particles through co-precipitation route and studied their thermal stability [6]. Ang et al. have prepared PZT thin films through sol-gel method and studied their dielectric responses [8]. Similarly, PZT particles have been prepared by other researchers through different routes whereas the current investigation is based on a simple, low cost, and environmental friendly high temperature solid state route [17–21].

This paper reports the preparation of $PbZr_{0.52}Ti_{0.48}O_3$ (PZT 52/48) nanoparticles through high temperature solid state reaction using stoichiometric amount of TiO_2, $Zr(OH)_2$, and Pb_3O_4. The effect of process parameter like temperature on the crystal structure, morphology, electric modulus, and dielectric properties of PZT particles are discussed in detail.

2. Synthesis of $PbZr_{0.52}Ti_{0.48}O_3$ nanoparticles

$PbZr_{0.52}Ti_{0.48}O_3$ nanoparticles are prepared *via* high temperature solid state reaction using stoichiometric amount of anatase TiO_2, Pb_3O_4 [Merck chemical Ltd., India], and $Zr(OH)_2$ [Loba chemie, India). All ingredients were dried at 120 °C for 6 h to remove the adsorbed moisture and then thoroughly mixed using an agate mortar and loaded in an alumina crucible. The mixture was heated in a furnace at 700 °C for 6 h and 1000 °C for 3 h followed by heating at 1200 °C (twice) for 6 h and 3 h respectively with three intermittent grindings. The powder obtained was grinded thoroughly by agate mortar before further study.

3. Characterization

The crystal structure of PZT particles prepared at different temperatures were characterized by X-ray diffractometer (model