Available online at www.sciencedirect.com
ScienceDirect
Ceramics International 41 (2015) 2774–2778
CERAMICS INTERNATIONAL
www.elsevier.com/locate/ceramint

The effect of Li_2CO_3 addition on the structural, dielectric and piezoelectric properties of PZT ceramics

Vineet Tiwari, Geetika Srivastava*

Department of Physics and Materials Science & Engineering, Jaypee Institute of Information Technology, Noida 201307, India

Received 9 September 2014; received in revised form 16 October 2014; accepted 17 October 2014
Available online 24 October 2014

Abstract

A detailed systematic study of the effect of Li_2CO_3 addition on the structural, dielectric and piezoelectric properties of the PZT (Zr/Ti $=50/50$) ceramics in the morphotropic phase boundary (MPB) region was carried out. The addition of Li_2CO_3 in the PZT system resulted in the improved sinterability and densification of the ceramics. 0.2 wt% Li_2CO_3 addition was found to be optimum for obtaining better dielectric and piezoelectric properties in the PZT ceramics. It was further seen that the addition of Li_2CO_3 shifted the MPB of the ceramics towards the tetragonal phase. The Zr/Ti ratio was hence, varied to regain the MPB in the PZT ceramics with an intention to obtain superior dielectric and piezoelectric properties.

Keywords: Dielectric; PZT; Piezoelectric; morphotropic phase boundary (MPB)

1. Introduction

Lead based perovskites form an important class of ferroelectrics. They have been widely investigated for their technological properties like high dielectric constant and piezoelectric coefficient which make them excellent candidates for device applications such as multilayer capacitors, transducers and actuators [1–3]. The $Pb(Zr_xTi_{1-x})O_3$ system and its modified solid solutions are known to exhibit excellent dielectric, elastic and piezoelectric properties at the 'Morphotropic Phase Boundary (MPB)' [4–7]. This MPB is believed to be a coexistence region of two phases namely, tetragonal and monoclinic phases and still is a topic of great debate [8–16].

The processing of these perovskites requires sintering at high temperatures above 1280 °C which limits their use in device applications. The high firing temperature results in the compositional fluctuation due to the evaporation of PbO and it not only deteriorates the electromechanical, piezoelectric, dielectric properties but also causes the environmental pollution. Further, the application of these materials in multilayer piezoelectric devices requires the sintering temperatures below 1000 °C in order to reduce the cost of expensive electrodes like platinum and palladium [17,18]. The high firing temperature is undesirable for Ag/Pd electrodes as the diffusion of Ag leads to the deterioration in the performance of the device due to the formation of interfacial microdefects. Thus, it is desired to lower the sintering temperature for the improved, reliable and reproducible material properties of these ceramics. Some of the methods employed for achieving low sintering temperature without forfeiting the properties of materials include the use of ultra fine powder [19], liquid phase sintering [20], use of additives [21], hot pressing [22] which enhance the solid state sintering. The use of additives with low melting point also known as sintering aids have been widely explored as they generally melt to form liquid at lower temperatures than the sintering temperature and promotes densification by the transportation of mass and reprecipitation. [23].

The lowering of sintering temperature in these lead based ceramics could be achieved by the addition of various metal oxides such as CuO, ZnO, Bi_2O_3, $LiBiO_2$ (LBO), Fe_2O_3, Li_2CO_3 and has been reported earlier [23–32]. Generally, the addition of these oxides led to the deterioration of piezoelectric properties or the sintering temperature could not be reduced

---

*Corresponding author. Tel.: +91 120 2594386; fax: +91 120 2400986.
E-mail address: geetika.srivastava@jiit.ac.in (G. Srivastava).

http://dx.doi.org/10.1016/j.ceramint.2014.10.096
0272-8842/

much. Hence, efforts have been made in the direction to reduce the sintering temperature of these ceramics without degrading the material properties.

Fan et al. recently investigated the influence of Li_2CO_3 and Sm_2O_3 additives on PZT-PZN ceramics. The sintering temperature was found to reduce to 950 °C without much degradation in the piezoelectric properties of the ceramics [25]. Liang et al. studied the effect of LBO addition on $Pb_{0.87}La_{0.03}(Zr_{0.53}Ti0_{.43})_{0.9925}O_3$ and found that by controlling the soaking time and concentration of LBO, these ceramics could be sintered at 950 °C and yielded high S_{11} of 0.22% under 3 kV/mm [27]. Sen et al. also tried LBO as a sintering aid and could sinter PZT ceramics at 'ultra' low temperature 750 °C though the synthesis method adopted was intricate and sensitive [29]. Hayashi et al. had also explored LBO as a sintering aid for various lead based PZT system [31,32]. Wang et al. synthesized PZT–Pb(Zn,Sb)–Pb(Ni,Te)O_3 ceramics at 980 °C using Li_2CO_3–Bi_2O–$CdCO_3$ as sintering aid and found that k_p of the sintered ceramics to be as high as 0.71 [23].

It has been seen from the literature that Li_2CO_3 is one of the most commonly used sintering aids for the synthesis of PZT based solid solutions. However, the effect of Li addition on the structural and material properties of PZT system has not been explored in detail. In this work, we have adopted our low temperature calcination route to synthesize PZT ceramics which results in fine particles thereby making the sintering mechanism easier [33,34]. Further, a detailed and systematic investigation is carried out to study the effect of Li_2CO_3 addition on the sinterability, structural, dielectric and piezoelectric properties of the PZT system. Since, Zr/Ti ratio plays a crucial role in deciding the phases and hence, the material properties of the PZT based system, therefore, Zr/Ti ratio is chosen to be 50/50 and later tailored to regain the MPB in the Li added PZT system with an objective to obtain superior dielectric and piezoelectric properties.

2. Materials and Methods

The nominal composition of $PbZr_{0.5}Ti_{0.5}O_3$ was synthesized by two-step solid-state reaction via low temperature calcination method [33]. The analytical grade of raw materials such as PbO, ZrO_2 and TiO_2 were taken in stoichiometric ratio, mixed in ethanol medium and were kept for calcination at 700 °C for an hour. 0.1, 0.2 and 0.3 wt% of Li_2CO_3 was added in the solution form to the nominal composition after the calcination stage and was preheated at 500 °C to remove all the volatile components. These powders were pelletized and kept at different sintering temperatures from 900 °C to 1280 °C in a lead controlled atmosphere. X-ray diffraction data were collected on the ceramic samples at normal scanning rate of 1°/minute, with a step size of 0.02° using Philips diffractometer. The densities of all the sintered samples were determined using modified three weight Archimedes' principle. The sintered pellets were polished and were gold coated. The electrical properties such as dielectric constant, dielectric loss of the sintered pellets were measured using HP – 4194 impedance/ gain-phase analyzer. The gold coated sintered ceramics were poled in silicone oil bath close to 300 °C by applying a dc electric field of 2KV/cm and cooling down to room temperature for the characterization of piezoelectric coupling coefficient d_{33}. The ceramics were aged for 24 hours prior to their measurements. The values of d_{33} were obtained using a Berlincourt Piezo d_{33} meter.

3. Results and discussions

3.1. Density measurements

Fig. 1 shows the variation of relative density of PZT ceramics with the sintering temperature and the amount of Li_2CO_3 added to the system. It can be seen from the figure that the densification of PZT ceramics could only be achieved at 1280 °C with the maximum density of 85% of the theoretical density. However the densification and sinterability was found to improve with the incorporation of Li^+ ions in the system. The increase in the density is attributed to the addition of Li_2CO_3 as sintering aid, which promoted liquid phase sintering. This liquid phase sintering not only resulted in the improved sinterability and densification of PZT powders but also helped in lowering the sintering temperature. The maximum density of 92% of the theoretical density was obtained for 0.2 wt% Li_2CO_3 added PZT samples and the sintering temperature could be lowered to 1000 °C as compared to the maximum relative density of 88% for 0.1 wt% Li_2CO_3 added systems at 1100 °C. It could be seen from the figure that the high amount of sintering aid beyond 0.2 wt% of Li_2CO_3 in the system did not further improve the density or lower the sintering temperature.

3.2. X-ray diffraction profile

The X-ray diffraction patterns of all the sintered ceramics showed the formation of a pure perovskite phase with no impurity peaks observed within the limit of X-ray detection. It is known that the (2 0 0) pseudocubic reflection is splitted into two peaks for tetragonal phase while the triplet splitting of this reflection is an indication of the presence of both monoclinic

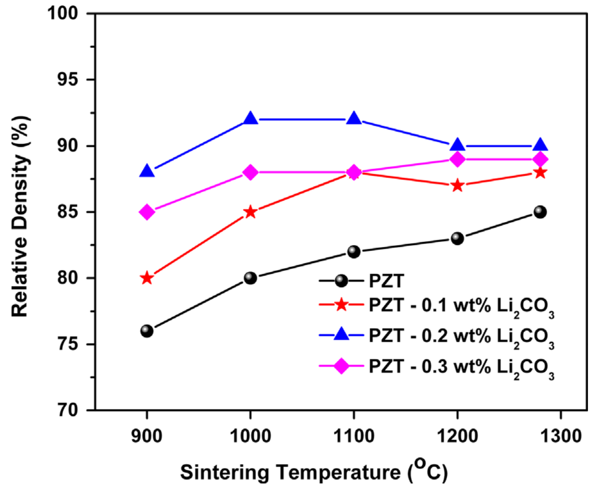

Fig. 1. The variation of relative density (%) with the sintering temperature for various wt% of Li_2CO_3 added PZT ceramics.