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Phase-formation, microstructure, and piezoelectric/dielectric properties of $BiYO_3$-doped $Pb(Zr_{0.53}Ti_{0.47})O_3$ for piezoelectric energy harvesting devices

Man-Soon Yoon, Iqbal Mahmud, Soon-Chul Ur*

Department of Materials Science and Engineering/RIC-ReSEM, Korea National University of Transportation, 50 Daehangno, Chungju, Chungbuk 380-702, Republic of Korea

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Abstract

This paper proposes a method for the composition and synthesis of lead zirconate titanate (PZT) piezoelectric ceramic for use in energy harvesting systems. The proposed material consists of $(1-x)Pb(Zr_{0.53}Ti_{0.47})O_3$–$xBiYO_3$ [PZT–BY(x)] ($x=0$, 0.01, 0.02, 0.03, 0.04, and 0.05 mol) ceramics near the morphotropic phase boundary (MPB) region, prepared by a solid-state mixed-oxide method. The optimum sintering temperature was found to be 1160 °C, which produced high relative density for all specimens (96% of the theoretical density). Second phases were found to precipitate in the composition containing $x\geq0.01$ mol of BY. It is shown that the addition of BY inhibits grain growth, and exhibits a denser and finer microstructure than those in the un-doped state. Fracture surface observation revealed predominant intergranular fracture for $x=0$ and $x=0.01$, while a mixed mode of transgranular and intergranular fracture appeared for $x\geq0.02$. The optimal doping level was found to be $x=0.01$, for which a dielectric constant (K_{33}^T) of 750, a Curie temperature (T_C) of 373 °C, a remnant polarization (P_r) of 50 μC/cm^2, a piezoelectric constant (d_{33}) of 350 pC/N, and an electro-mechanical coupling factor (k_p) of 65% were obtained. In addition, the piezoelectric voltage constant (g_{33}), and transduction coefficient ($d_{33}\times g_{33}$) of PZT–BY(x) ceramics have been calculated. The ceramic PZT–BY(0.01) shows a considerably lower K_{33}^T value, but higher d_{33} and k_p. Therefore, the maximum transduction coefficient ($d_{33}\times g_{33}$) of 18,549 × 10^{-15} m^2/N was obtained for PZT–BY(0.01). The large ($d_{33}\times g_{33}$) indicates that the PZT–BY(0.01) ceramic is a good candidate material for energy harvesting devices.

Keywords: A. Sintering; B. Grain size; D. PZT; Energy harvesting

1. Introduction

Recently, energy harvesting from vibration and motion sources has attracted much interest, particularly for micro power sources [1,2]. To convert this mechanical energy to electrical energy, vibration energy harvesters use one of three methods: electrostatic induction, electromagnetic induction, and the piezoelectric effect [3,4]. Among these transducers, piezoelectric harvesters are preferred due to their simplicity, easy maintenance, and durability. Depending on the given application, high power density is required in piezoelectric technology, for which a large electro-mechanical coupling effect is required [5,6]. In addition, systems should be much simpler, without external voltage sources. Lead zirconate titanate (PZT) has relevant piezoelectric properties, and is usually used as an energy conversion material in piezoelectric structures. Numerous relevant studies on piezoelectric harvesters have been performed in the last decade [7–10]. Suitable piezoelectric materials for vibration energy conversion to electrical energy are characterized by a large magnitude of the product of the piezoelectric voltage constant (g_{33}) and the piezoelectric charge constant (d_{33}), which is called the transduction coefficient ($d_{33}\times g_{33}$) [11–13]. Recently, many studies have been conducted to find such piezoelectric materials [11–14]. According to the definition of g_{33} expressed by $d_{33}/(\varepsilon_0\times K_{33}^T)$ (where K_{33}^T is the dielectric constant and ε_0 is dielectric permittivity of free space), a high energy density could be obtained from piezoelectric materials with a large d_{33} value and small K_{33}^T. A higher product of d_{33} and g_{33}, i.e., a higher figure of merit ($d_{33}\times g_{33}$), can provide higher energy output, and hence, the value is an essential criterion for energy

*Corresponding author. Tel.: +82 43 841 5385; fax: +82 43 841 5380.
E-mail addresses: scur@ut.ac.kr, urwin@hanmail.net (C. Ur).

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harvesting materials [15,16]. Many investigations have been conducted to obtain piezoelectric ceramics with a high d_{33} value and small K_{33}^{T} [17–19].

From considerations of ionic radii, it is probable that bismuth (Bi) and yttria (Y) ions occupy the Pb site, and that charge compensation will take place by the creation of Pb vacancies in the lattice, which facilitate the movement of the domain wall so as to improve the piezoelectric and dielectric properties [20–25]. It was reported that the substitution of Bi in PZT increased sinterability, retarded grain growth, and decreased grain size [22–24]. In addition, it was also reported that a uniform grain size distribution with decreasing grain size yielded a large P_r and a small leakage current in Y-doped PZT materials [20,21,25]. Bi and/or Y doping in PZT would be expected to increase d_{33} and K_{33}^{T} but decrease the g_{33} value. Since $BiYO_3$ (BY) generally shows a low dielectric constant, one can predict that pre-synthesized BY can act as a dopant to reduce the dielectric constant in PZT. A preliminary study indicated that pre-synthesized BY doped into PZT could remain as a precipitate after sintering, according to X-ray diffraction analysis. This implies that BY can act as a grain growth inhibitor and as donors in the vicinity of grains. Thus, the existence of BY precipitate can have an influence on the grain growth and the piezoelectric and dielectric properties, in contrast to direct doping methods.

The main purpose of the present study is to demonstrate the possibility of optimum energy harvesting material with a high figure of merit ($d_{33} \times g_{33}$) by controlling the pre-synthesized BY contents. To this end, we investigate the effect of pre-synthesized BY content on the crystal structure and microstructure, and analyze the piezoelectric/dielectric properties in the PZT–BY system to search for the optimum compositions with high d_{33} and low K_{33}^{T}.

2. Experimental procedure

A conventional mixed oxide method was used to fabricate $(1-x)Pb(Zr_{0.53}Ti_{0.47})O_3$–$xBiYO_3$ (abbreviated as PZT–BY(x) hereafter) containing various amounts of BY ($0 \le x \le 0.05$). To eliminate the effects associated with the direct co-doping of Bi_2O_3 and Y_2O_3, a pre-synthesis method was used for the fabrication of PZT–BY(x) by a ball mill process. The first stage of the fabrication was the synthesis of PZT and BY. A stoichiometric amount of analytical-reagent (AR)-grade PbO (99.5%, Dansuk, Korea), ZrO_2 (99.5%, Daichi, Japan), and TiO_2 (99.9%, High purity Chemicals, Japan) to synthesize PZT; and Bi_2O_3 (99.9%, High purity Chemicals, Japan) and Y_2O_3 (99.9%, High purity Chemicals, Japan) to synthesize BY were weighed and then ball milled in distilled water using ZrO_2 media for 24 h. The dried powders were discretely sieved through 100 mesh and separately calcined at 850 °C for 2 h in alumina crucibles. X-ray analysis at this stage indicated a single phase. The second stage the PZT–BY(x) was fabricated by first weighing the pre-synthesized PZT and BY powders and ball-milling them for 72 h. The dried powders were pressed into a 15-mm-diameter disk and then subjected to cold isostatic pressing (CIP) under a pressure of 147.2 MPa. The pressed pellets were sintered at various temperatures. To limit PbO loss from pellets, a PbO-rich atmosphere was maintained by placing an equimolar mixture of PbO and ZrO_2 inside a covered alumina crucible. The sintered specimens were then ground to maintain the required aspect ratio (diameter/thickness ≥15) with an average diameter of 11.7 mm and thickness of 0.75 mm for measuring the radial vibration mode of the piezoelectric properties. In addition to this, a cube sample with an edge length of 10 mm was also prepared to measure the d_{31} value following measuring instruction of a d_{33}/d_{31} meter (IACAS; Model ZJ-6B) at the optimum composition.

A preliminary study on the dielectric/piezoelectric properties of the PZT–BY(x) system indicated that the 0.99Pb$(Zr_{0.53}Ti_{0.47})O_3$–$0.01BiYO_3$ composition had excellent dielectric/piezoelectric properties. Thus, specimens with the same composition were prepared by conventional mixed-oxide method without a pre-synthesizing process to investigate the processing effects. A stoichiometric amount of the AR-grade powders were simultaneously mixed and dried. The dried powder was calcined at 850 °C for 2 h.

The specimens were characterized by X-ray diffractometer (XRD, Rigaku D/Max-2500H, Japan) with Cu Kα radiation after calcination and sintering. The morphologies and microstructures of all of the powders and sintered samples were investigated using a scanning electron microscope (SEM; Hitachi S-2400). In order to measure the electrical properties, silver paste was coated to form electrodes on both sides of the sample, and then subsequently fired at 560 °C for 30 min. To investigate the proper poling conditions, each specimen was poled in stirred silicon oil at 120 °C, by applying a DC electric field of 4–8 kV/mm for 45 min, and subsequent aging at 120 °C for 3 h. Preliminary study indicated that the spontaneous polarization was not fully saturated under a DC electric field of 4 kV/mm. The dielectric and the piezoelectric properties of the aged samples were then measured and evaluated. Based on these results, the optimum poling voltage chosen as 4.0 kV/mm. Considering the fact that deviations of the electric properties could exist in the measured samples, five specimens were prepared and tested for each batch. The piezoelectric coefficient was determined using a d_{33}/d_{31} meter (IACAS; Model ZJ-6B), and the electromechanical and dielectric properties were calculated by a resonance/anti-resonance measurement method [26] using an impedance/gain phase analyzer (HP-4194A). The temperature dependence of the dielectric constant and the dissipation factor over a range of −25 to 500 °C was measured using an automated system at 1 kHz, in which an HP-4194A Impedance/Gain-Phase Analyzer and a temperature-control box (−40 to 150 °C: Delta 9023 chamber, 150–500 °C: Lindberg tube furnace) were controlled by a computer system. The temperature was measured using a Keithley 740 thermometer with a K-type thermocouple mounted on the samples. The behavior of the polarization electric field was determined using a Precision LC system (Radiant Technology Model: 610E).

3. Results and discussions

3.1. Effects of pre-synthesized $BiYO_3$ doping on the crystal structure and microstructure

Fig. 1 shows the XRD patterns for the calcined BY and PZT. A full stabilization of the cubic phase was achieved for the BY (JCPDS no. 271047), as shown in Fig. 1(a). In