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Enhanced Piezoelectric Properties and Tunability of Lead-Free Ceramics Prepared by High-Energy Ball Milling

M.L.V. MAHESH,[1,2] V.V. BHANUPRASAD,[1] and A.R. JAMES[1]

1.—Ceramics and Composites Group, Defence Metallurgical Research Laboratory, Hyderabad 500 058, India. 2.—e-mail: mahesh.mlv@gmail.com

Zirconium-doped barium titanate $Ba(Zr_{0.15}Ti_{0.85})O_3$ lead-free ceramics (hereinafter referred to as BZT) were synthesized using the solid-state reaction method by adopting the high-energy ball milling technique. Nanosized BZT powders resulted from high-energy ball milling, which in turn enhanced the dielectric and piezoelectric properties of the ceramics. A single-phase perovskite structure free from secondary phase peaks was observed for sintered BZT samples, and a relative density of ~94% of the theoretical density was achieved. The electric-field-induced polarization-current data indicate the ferroelectric nature of the samples. Unipolar strain as high as 0.12% was realized for the ceramics sintered at 1350°C, indicating their potential for use in actuator applications. Very high tunability of >70% for these ceramics is also reported.

Key words: Ceramics, electronic materials, piezoelectricity, dielectric properties

INTRODUCTION

$BaTiO_3$ (BT) is the most promising lead-free material, exhibiting superior properties such as high dielectric permittivity, low dielectric loss tangent, dielectric reliability, high electromechanical coupling coefficients, good thermal shock resistance, and large tunability.[1] Hence, this material finds applications in thermistor and tunable microwave device applications, etc.[2,3] A lot of work has been carried out to evaluate the properties of doped BT ceramics.[4,5] For such ABO_3-type perovskites it is reported that B-site dopants such as Sn and Zr decrease the phase-transition temperature.[5] Zr is chosen in this study as a dopant due to its effective role in minimizing the dielectric loss at low frequencies.

Different routes have been adopted to prepare $Ba(Zr_xTi_{1-x})O_3$ powders (BZT), including sol–gel,[6] high-energy ball milling,[7] Pechini method,[8] templated grain growth,[9] citrate method,[10] oxalate method,[11] hydrothermal processing,[12] coprecipitation technique,[13] etc. Of all these methods, ball milling is widely adopted due to its advantages such as the low cost of starting materials, relatively simple operation, processing at room temperature, etc. Also, processing via other methods requires high calcination temperatures, which result in increased particle sizes. Table I presents a compilation of the reported literature on $Ba(Zr_xTi_{1-x})O_3$ ceramics that were processed using the high-energy ball milling technique. It can be noted from Table I that previous researchers carried out milling for prolonged durations;[14–19] e.g., Kong et al.[20] reported an increase in dielectric loss with increased duration of milling.

EXPERIMENTAL PROCEDURES

Ceramic compacts of $Ba(Zr_{0.15}Ti_{0.85})O_3$ powders were synthesized by solid-state reaction using high-energy planetary ball milling. The raw materials of analytical reagent (AR) grade (all of M/s. Sigma Aldrich, USA) $BaCO_3$ (99%), TiO_2 (99.9%), and ZrO_2 (99%) were weighed in appropriate proportions according to the stoichiometric ratio and then homogeneously mixed with distilled water in zirconia vials with balls of 3 mm diameter. Milling was performed at speed of 150 rpm for 5 h with the mill

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