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Effect of preparation methods on properties of barium zirconium titanate ceramics

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Abstract

Barium zirconium titanate ceramics in a composition of $BaZr_{0.09}Ti_{0.91}O_3$ were synthesized from powders prepared by a conventional mixed oxide and vibro-milling methods. Properties of the ceramics were investigated. Compared to a conventional sample, the ceramic prepared using the vibro-milling method showed a higher dielectric constant and better dielectric responds under high electric fields. The microstructural properties of the samples were investigated. It was proposed that the densification and microstructure of the ceramics were responsible for the improvement of the ceramics properties.

Keywords: Ceramics, Dielectric properties, Microstructure, Densification

INTRODUCTION

Barium titanate ($BaTiO_3$) is a ferroelectric (FE) material which has a perovskite structure. $BaTiO_3$ and $BaTiO_3$ based (modified $BaTiO_3$) are widely used as capacitors due to their high dielectric constant (Uchino, 1996). These materials are also the promising candidates for environmental friendly ferroelectric or piezoelectric materials as they have no toxic element such as lead oxide which is easily volatile during processing. (Wang *et al*., 2006). Recently, it was reported that barium zirconate titanate ($Ba(Ti_{1-x}Zr_x)O_3$, BZT) exhibited high dielectric and piezoelectric properties. This material is also considerable to be one of the most important lead free $BaTiO_3$-based ceramics where it is also a lead free ceramic. However, electrical properties of the pure BZT ceramics are lower than that found in many lead –based ceramics such as lead zirconate titanate ($Pb(Ti_{1-x}Zr_x)O_3$, PZT). Therefore, various techniques have been proposed to improve the electrical properties of the BZT ceramics (Yu *et al*., 2002). Many authors have suggested that properties of BZT ceramics depended on many factors such as microstructures and dopants (Tanmoy *et al*., 2006). Further, properties of the ceramics also depend on method of preparation. Relations between these factors and their properties have been extensively studied (Kong *et al.*, 2008). It is also known that better performance of the ceramics requires a high quality of starting powder. Various approached have been proposed to synthesize the BZT powders. The conventional mixed-oxide method has been often applied to synthesized BZT powders. However, this method produces coarsening and aggregation of the powders and requires a high calcination temperature. Other chemical routes including sol-gel process and hydrothermal and microwave synthesis have been reported for producing the fine BZT powders (Tang *et al.*, 2005). However, the yield product that obtained from these methods is so small and the costs of raw materials for these routes are rather high. Recently, it is reported that vibro-milling method is an effective technique to produce a fine ceramic power as a result in improvement of many ceramic properties (Khamman *et al.*, 2006). In the present work, effects of vibro-milling on the property and microstructure of $BaZr_{0.09}Ti_{0.91}O_3$ ceramics were investigated. The results were compared to the ceramics prepared by a conventional ball-milling method.

EXPERIMENTAL PROCEDURE

The metal oxide powders, $BaCO_3$, TiO_2 and ZrO_2, were weighed based on the stoichiometric formula of $BaZr_{0.09}Ti_{0.91}O_3$. The metal oxide powders were mixed in isopropanol. In this work, two ball mill techniques, i.e., conventional ball mill and vibro-milling methods were performed. The ball milled powders were dried, ground using a mortar and pestle and then sieved before calcining for 2 h at 1250 ^oC, with a heating/cooling rate of 1.67 $^oC/min$. The obtained powders were mixed with polyvinyl alcohol (PVA) binder for 3wt.% by a conventional ball milling method for 24 h in ethanol. The resulted powders were pressed into disc-shape pellets with 10 mm in diameter and 3 mm in thickness. The green disc pellets were sintered at temperatures ranging from 1150 ^oC to 1450 ^oC for 2 h. Phase formation was determined by X-ray diffraction analysis (XRD), using a diffractometer with CuK_α radiation. The density of the samples was determined using the Archimedes method with distilled water as the fluid media. Morphology of the mixed starting powder and ceramics were studied by a scanning electron microscope (SEM). For the electrical measurements, fired-on silver electrodes were applied to both sides of the pellets which had been ground to a thickness of 1.0 mm. The mechanical properties of the ceramics were determined by a Vickers hardness tester.

RESULTS AND DISCUSSION

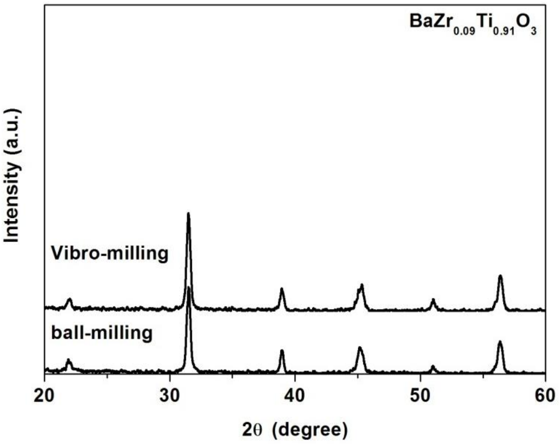


Figure 1 XRD patterns of $BaZr_{0.09}Ti_{0.91}O_3$ prepared from different techniques.

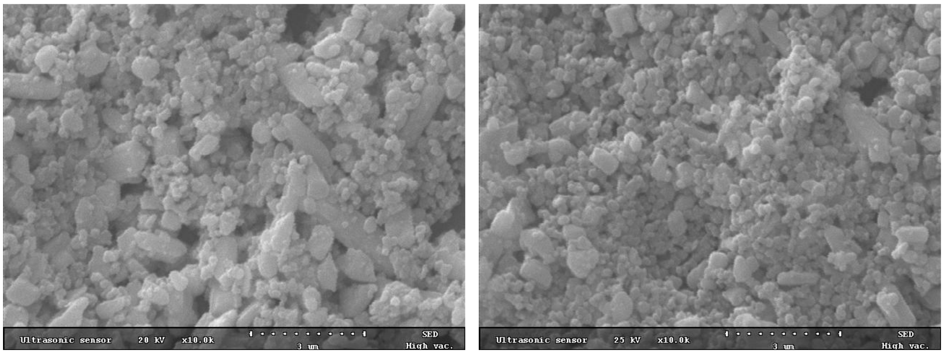
To determine the phase formation, the ceramics were examined by XRD at room temperature. XRD diffraction patterns of the samples prepared by conventional and vibro-milling methods are shown in Figure 1. From the XRD data, all of the main diffraction peaks correspond to an orthorhombic symmetry which is indicative of a ferroelectric phase (Jarupoom *et al*., 2010). Additionally, the XRD result shows that both samples exhibit a pure perovskite phase. There is no evidence of impurity product in the XRD patterns of both samples, suggesting that phase formation of the samples was not influenced by the method of milling.

To study the influence of preparation methods on the densification, density of the ceramics was determined. It was found that the density of the vibro- milling ceramic was higher than that obtained from the conventional ball-mill ceramic. By using Archimedes method, density of conventional ball-milling and vibro- milling ceramics were 5.64 and 5.83 g/cm^3, respectively (Table 1). Linear shrinkage of the ceramics was also determined and the results are shown in Table 1. The linear shrinkage for the vibro- milling sample is 14.50% which slightly higher than that obtained from the conventional ball-mill sample (14.37%). These results indicate that vibro- milling produced a better sinterability of the ceramics.

Table 1 Properties of $BaZr_{0.09}Ti_{0.91}O_3$ ceramics prepared by conventional ball-milling and vibro-milling methods.

Milling method	Density (g/cm^3)	Linear Shrinkage (%)	Average Particle size (µm)	Average Grain size (µm)	Dielectric constant@1kHz	Loss tangent @1kHz	Hardness (GPa)
Conventional	5.64	14.37	0.356	22.23	1622	0.012	4.81
Vibro-milling	5.83	14.50	0.289	20.51	1465	0.017	4.66

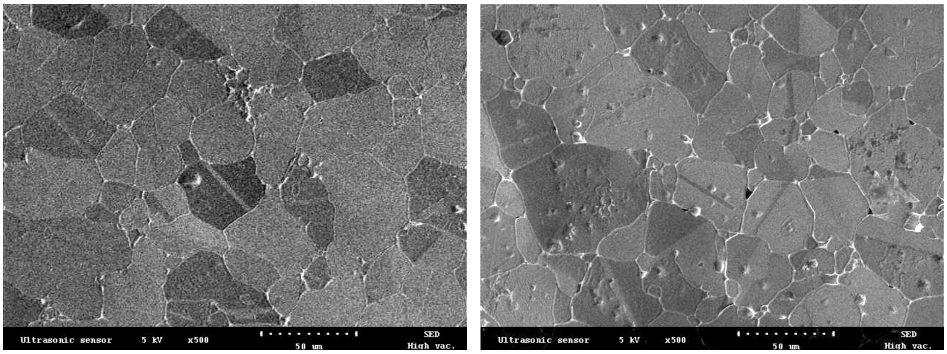
Morphology of the raw materials after milling, showed that the vibro-milling produced finer particles, comparing to that of conventional milling (Figures 2(a) and(b)).The average particle sizes were determined to be 0.356 and 0.289 μm for the conventional and vibro- milling samples, respectively. It is known that a finer particle powder leads to higher chemical reaction efficiency as a result of the lower calcination temperature. Therefore, better properties should be obtained from the ceramic prepared by vibro-milling method.



(a) (b)

Figure 2 Morphology of $BaZr_{0.09}Ti_{0.91}O_3$ powders before calcination : (a) conventional ball-milling (b) vibro-milling.

Figure 3 illustrated the microstructures of the ceramic samples. The average grain sizes, as calculated from the intercept method, were 22.23 and 20.51 μm for the conventional and vibro-milling samples, respectively. It should be noted that the vibro-milling ceramic exhibits a non-uniform in grain size comparing to the conventional sample. This characteristic may result in the lower average grain size for the vibro-milling ceramic. It is believed that the vibro-milling which is a high energy milling could produce non uniform particle sizes, leading the fluctuation of grain growth mechanism in some area during sintering. The occurrence of non-uniform grain size was then clear evident in the vibro-milling sample.



(a) (b)

Figure 3 Microstructure of $BaZr_{0.09}Ti_{0.91}O_3$ ceramics: (a) conventional ballmilling (b) vibro-milling.

Figure 4 shows the dielectric constant of the ceramics as a function of frequency over a range of 100 – 1MHz. Both samples exhibit dielectric constant stability over the measured frequency range. However, the vibro-milling ceramic exhibits a higher dielectric constant, comparing to the conventional ceramic. Loss tangent values of the ceramics are listed in Table 1. All ceramic samples show low loss tangent value, suggesting that these ceramics are suitable for capacitor applications. There is no significant difference in this value for both ceramics (Table 1). To study the effect of electric field on dielectric constant of the ceramics, dielectric constant as a function of electric field were determined. Figure 5 shows the dielectric behavior of the ceramics under the applied electric fields. It can be seen that the dielectric constants for both ceramics decrease with increasing the electric fields. In addition, the dielectric responds under applied electric fields for the vibro-milling ceramic is higher than that of conventional ceramic. It should be noted that the improvement of the dielectric properties for the vibro-milling sample in this work can be related to its high densification, i.e., the higher density gave the higher dielectric constant.

Normally, BZT ceramics can be applied for electronic applications. Therefore, their electrical properties were always investigated. However, mechanical properties of these materials should also be considered for the applications under large applied electric fields. In that the ceramics should be resistant to microcracking or fracture toughness when they are subjected to the high electric field. Therefore, mechanical property of the ceramics: Vickers hardness was determined in this work. The values of hardness are tabulated in Table 1. It can be seen that the vibro-milling ceramics possess a slightly higher hardness value (4.81GPa) than that of the conventional ball-milling ceramic (4.66GPa). Reason for the higher hardness value in the vibro-milling ceramic can be link to its density and grain size. For example, a higher density results in a higher hardness value while a larger grain size produces a lower hardness.

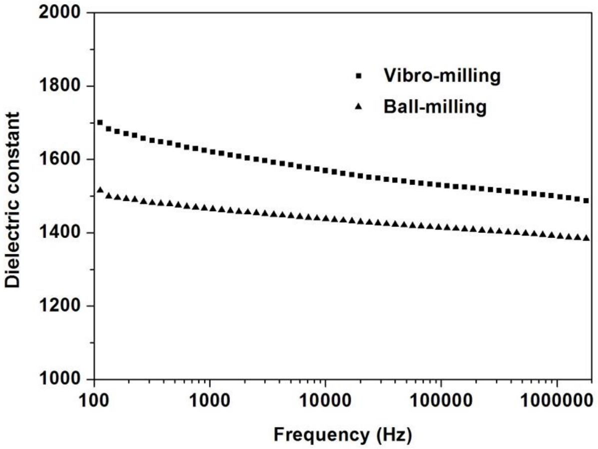


Figure 4 Dielectric constant as a function of frequency for the $BaZr_{0.09}Ti_{0.91}O_3$ ceramics.

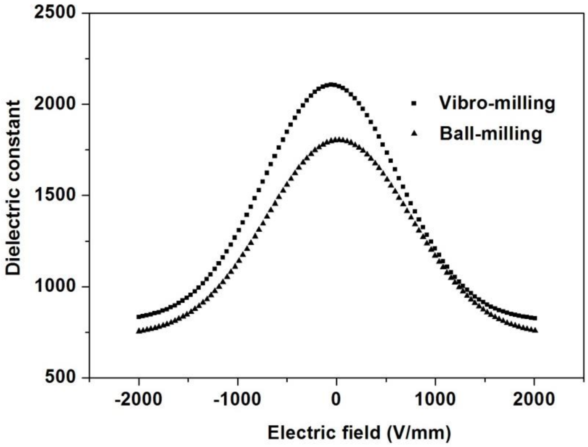


Figure 5 Dielectric constant as a function of applied electric field for the $BaZr_{0.09}Ti_{0.91}O_3$ ceramics.

CONCLUSIONS

Effects of milling methods, conventional and vibro-milling, on the properties of $BaZr_{0.09}Ti_{0.91}O_3$ ceramics were demonstrated in the present work. Compared properties of both ceramics were reported. The vibro-milling ceramic exhibited higher dielectric properties and better electric fields respond. Further, the vibro-milling ceramic also showed a better mechanical property. The densification and microstructure of the ceramics were proposed to respond for the enhanced ceramic properties.

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