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The formation of Y5V-type fine-grained ceramics based on spherical submicron $BaZr_{0.1}Ti_{0.9}O_3@Al_2O_3$ particles

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ABSTRACT

To improve multilayer ceramic capacitors (MLCCs), thinner dielectric layers are necessary. To achieve this goal, both grain size and uniformity of the MLCC particles must be controlled effectively. In this study, the core-shell structure of submicron-sized multi-function ceramic capacitors powder was synthesized using a novel precipitation route, which controls both dispersion and particle size of $BaZr_{0.1}Ti_{0.9}O_3$ and $BaZr_{0.1}Ti_{0.9}O_3@Al_2O_3$ particles. In this paper, we investigate the effect of Al_2O_3 coating on the microstructure and the dielectric properties of $BaZr_{0.1}Ti_{0.9}O_3$. We found that both average grain size and maximum dielectric constant (ε_{max}) of the ceramics decrease with increasing concentration of Al_2O_3. Our results demonstrate that fine-grained ceramic materials can meet the specifications of the Electronic Industries Alliance Y5V with a concentration of Al_2O_3-coated of 0.25 mol percent, a permittivity of 3393 at room temperature, and an average particle size of about 400 nm.

1. Introduction

In the past decade, multilayer ceramic capacitors (MLCCs) could be improved considerably to meet the growing requirements for miniaturization [1,2]. MLCCs are typically produced from multiple dielectric layers, each of which must be 1 μm or less thick. This requires the use of superfine powder as starting material, and the homogeneity and the size of the particles to be controlled effectively [3]. To meet these demands, much attention has been paid to wet chemical synthesis methods such as precipitation or solvothermal approaches. Lee et al. [4] used a solvothermal method to prepare $BaTiO_3$ particles of about 100 nm diameter. Pithan et al. [5] prepared 200 nm $BaTiO_3$ particles via a solid-state method. Compared to the solid-state method, wet chemistry can potentially produce more uniform $BaTiO_3$-based ceramic powder that is suitable for use in MLCCs, with a particle size below 300 nm.

Barium zirconium titanate (BZT) ceramics are eco-friendly and lead-free ferroelectric materials with significant relaxor properties. Modified BZT composites are promising candidates for Y5V-type MLCCs [6] that comply with the Electronic Industries Alliance (EIA) code and Y5V specification ($-82\% \leq \varepsilon - \varepsilon_{25\,°C}/\varepsilon_{25\,°C} \leq 22\%$ between 30 and 85 °C). Solid solutions based on $Ba(Zr_xTi_{1-x})O_3$ have been studied widely because of their high maximum dielectric constant (ε_{max}), which is associated with a broad phase transition [7]. Furthermore, $Ba(Zr_xTi_{1-x})O_3$ ceramics show a broad dielectric peak near T_m (the temperature of maximum dielectric permittivity) due to the non-homogeneous distribution of Zr ions at Ti sites and because of the development of mechanical stress in the grain [8–10]. Doping of $Ba(Zr_xTi_{1-x})O_3$ ceramics has become a common method to improve the material [11]. Because of the compact structure, which can inhibit the motion of charge carriers, Al_2O_3 is an effective additive for the improvement of the dielectric properties of $Ba_{0.6}Sr_{0.4}TiO_3$ (BST) [12] and $Ba_{0.95}Ca_{0.05}Ti_{0.85}Zr_{0.15}O_3$ (BCTZ) ceramics [13]. Especially Al_2O_3, when uses as coating compound, can not only enhance the dielectric constant and reduce dielectric loss [13] but also inhibit subsequent grain growth [14,15]. Therefore, if Al_2O_3 is added into the BZT powder, the compromised state may not occur.

In this study, we developed a simple precipitation-based method for the synthesis of $BaZr_{0.1}Ti_{0.9}O_3$-based fine-grained ceramics, which have the potential to meet the Y5V specification. We selected submicron $BaZr_{0.1}Ti_{0.9}O_3$ particles for the core because of their high maximum dielectric constant (ε_{max}). We then prepared submicron-sized $BaZr_{0.1}Ti_{0.9}O_3$ powder using the hydrophase method at atmospheric pressure to control both dispersion and particle size. We then prepared $BaZr_{0.1}Ti_{0.9}O_3@Al_2O_3$ particles using precipitation-based coating. We investigated the effect of the Al_2O_3 coating on the microstructure, dielectric properties, and

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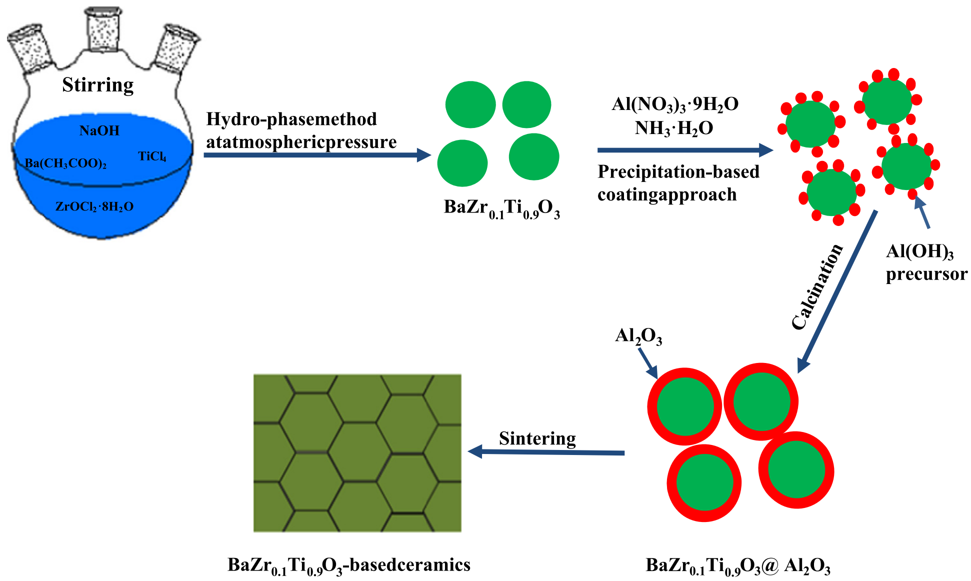

Fig. 1. Schematic illustration of the formation of fine-grained $BaZr_{0.1}Ti_{0.9}O_3$-based ceramics.

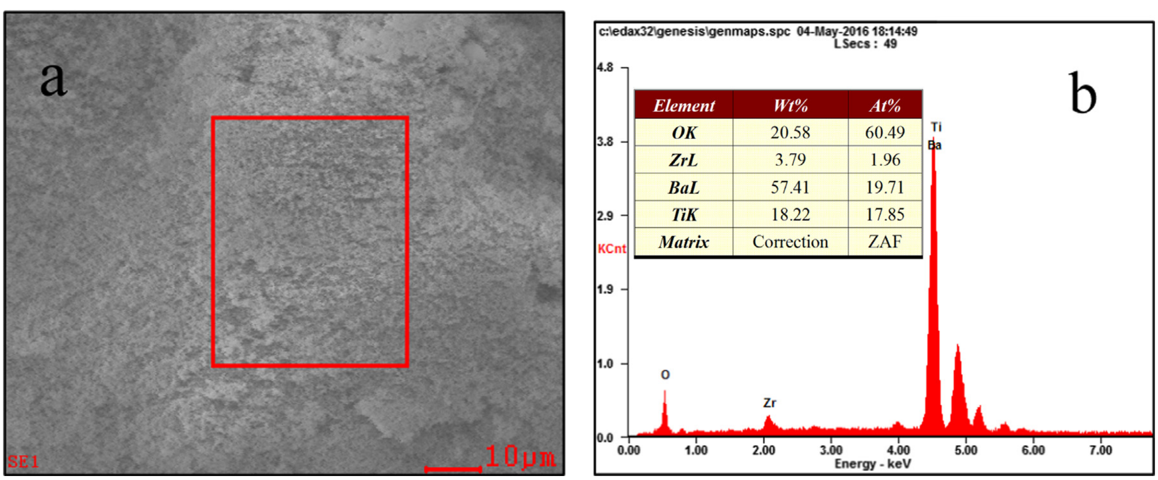

Fig. 2. (a) SEM images and (b) EDS analysis of $BaZr_{0.1}Ti_{0.9}O_3$ powder.

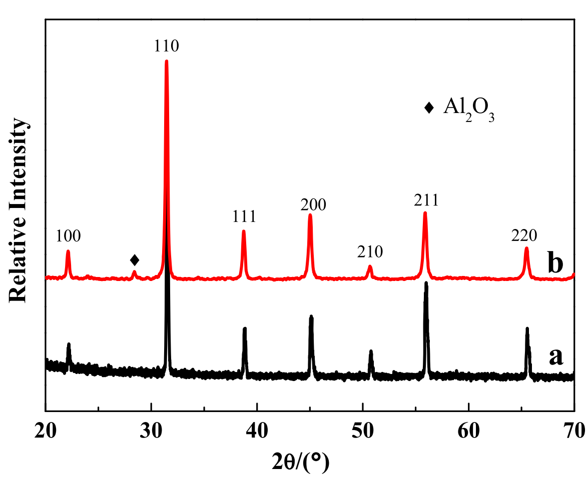

Fig. 3. XRD patterns for (a) $BaZr_{0.1}Ti_{0.9}O_3$, (b) $BaZr_{0.1}Ti_{0.9}O_3$ coated with 0.15 mol percent Al_2O_3.

the sintering of the resulting core–shell particles, to produce dense, fine-grained $BaZr_{0.1}Ti_{0.9}O_3$-based ceramics.

2. Experimental

$BaZr_{0.1}Ti_{0.9}O_3@Al_2O_3$ powder was synthesized by combining the hydro-phase method (at atmospheric pressure) with a precipitation-based coating approach. $BaZr_{0.1}Ti_{0.9}O_3$ powder was chosen for the core, Al_2O_3 powder for the shell, and sintering of the resulting core–shell particles to produce dense, fine-grained $BaZr_{0.1}Ti_{0.9}O_3$-based ceramics. A schematic of this process is shown in Fig. 1.

2.1. Synthesis of $BaZr_{0.1}Ti_{0.9}O_3@Al_2O_3$ particles

The ammonia solution was added to the monodispersed $BaZr_{0.1}Ti_{0.9}O_3$ slurry, it reacted with the aluminum nitrate solution to form an $Al(OH)_3$ layer on the surface of the monodispersed $BaZr_{0.1}Ti_{0.9}O_3$ particles. Heterogeneous nucleation of a solid phase from solution requires lower activation energy than homogeneous nucleation. This is because the energy of the solid–solid interface is lower than that of the solid–liquid interface [16–18]. Thus, the