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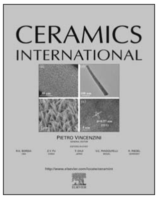

Fabrication of Y and Fe co-doped $BaZr_{0.13}Ti_{1.46}O_3$ fine-grained ceramics for temperature-stable multilayer ceramic capacitors

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ABSTRACT

Y^{3+} and Fe^{3+} co-doped $BaZr_{0.13}Ti_{1.46}O_3$ powders were synthesized by wet chemical method through a precipitation process, able to control uniformity and particle size of the $BaZr_{0.13}Ti_{1.46}O_3$-based particles. Fine-grained $BaZr_{0.13}Ti_{1.46}O_3$ ceramics co-doped with various amounts of Y^{3+} and Fe^{3+} were prepared at low sintering temperature to yield good dielectric properties and gentle temperature stability. The co-doping effect on the microstructure and dielectric properties of $BaZr_{0.13}Ti_{1.46}O_3$ ceramics were studied. Results showed the dielectric constants firstly to increase monotonically then decrease with the increase of Y^{3+} and Fe^{3+}concentration. Overall, the resulting ceramics met the X8R specification when Y^{3+} and Fe^{3+} contents were 2 or 4 mol%. Moreover, the increase in Y^{3+} and Fe^{3+} doping concentration from 6 to 8 mol% satisfied the X7R specification.

1. Introduction

Recently, the quest for improving multilayer ceramic capacitors (MLCCs) to meet the growing needs for miniaturization gained considerable attention. MLCCs are typically produced from multiple dielectric layers, in which the thickness of each layer must be 1 µm or less. Therefore, it is necessary to improve the synthetic methods of nano-sized or submicron-sized that will allow the production of fine-grained ceramics to meet the growing demand for high capacitance and miniaturization [1–5]. To satisfy these requirements, the wet chemical method [6–11] is an effective process when compared to traditional solid state processes [12–15]. This could effectively help the control over the dispersion and particle size of powders.

$BaZr_xTi_{1-x}O_3$ (BZT) ceramics have widely been used in electronic ceramic industry due to their excellent dielectric and ferroelectric properties, especially as Y5V-type multilayer ceramic capacitors [16–18]. The Y5V specification stands for $-82\% \le \varepsilon - \varepsilon_{25\,°C}/\varepsilon_{25\,°C} \le 22\%$ in the temperature range from −30 to 85 °C. However, the relatively high temperature coefficient of capacitance (TCC) of BZT ceramics in the temperature range from −55 to 150 °C has limited their applications in capacitors [19–21], and they did not meet the X7R or X8R specifications (X gives the minimum temperature of −55 °C, 7 or 8 means the maximum temperature (125 °C or 150 °C), while R symbolizes the percentage of capacitance variation being less than ± 15% over the whole temperature range, i.e.,$\triangle C/C \le \pm 15\%$). Materials with low TCC values are important for high-performance ceramic capacitors [22,23]. Therefore, it is desirable to develop BZT ceramics with broader temperature usage ranges, which could meet the requirements of MLCC at elevated temperatures. Different mechanisms dealing with the decrease in TCC have been proposed, specifically for $BaTiO_3$-based ceramics. The introduction of various additives allowed a flat temperature dependence of the dielectric constant [24,25].

Previous studies have shown that the addition of Y^{3+} may raise the dielectric permittivity and further broaden the dielectric peak [26–29]. On the other hand, the substitution of Fe^{3+} was found effective in enhancing the dielectric properties of ceramic materials [30–32]. Zuo et al. [33] and Cheng et al. [34] found that Fe^{3+} and rare earth co-doping may promote the densification process and improve the temperature stability of ceramics. Furthermore, most reported BZT ceramics require relatively high sintering temperatures of approximately 1300 °C. The average grain sizes of the obtained ceramics were found over 1 µm, which were pretty large for new MLCCs. Thus, excess TiO_2 led to the formation of liquid phase BZT with lower melting points, and therefore reduced the sintering temperature [35,36]. The incorporation of Y^{3+} [26] and Fe^{3+} [33,34] could replace Ti^{4+} to produce oxygen vacancies, so that the energy generated by the lattice

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distortion leads to segregation of the grain boundary and eventually inhibit the grain growth [10].

In this study, a simple system was developed to synthesize fine-grained BZT ceramics with temperature-stable dielectric properties at the lower sintering temperature. Submicron-sized Y^{3+} and Fe^{3+} co-doped BZT powders were prepared by a precipitation route, able to control their uniformity and particle size. The effects of added Y^{3+} and Fe^{3+} on the microstructure and dielectric properties of BZT ceramics were also examined.

2. Experimental

The starting materials used in the synthesis of the ceramics were $Ba(CH_3COO)_2$ (99% purity), $TiCl_4$ (99%), $Zr(NO_3)_4·5H_2O$ (99%), $Fe(NO_3)_3·9H_2O$ (99%), Y_2O_3 (99.9%), and NaOH (99%). Y_2O_3 was dissolved in nitric acid to produce a yttrium nitrate solution.

The $BaZr_{0.13}Ti_{1.46}O_3$ powders were prepared according to the literature [7]. Briefly, suspension slurries of 1.0 g BZT per 200 mL of water were prepared by means of ultrasonic dispersion for 0.5 h. The $Y(NO_3)_3$ and $Fe(NO_3)_3$ solution [n_Y: n_{Fe}=1:1] was then added to the BZT suspension slurries. Afterward, an ammonia solution was poured to the mixed slurry to adjust the pH value to 9.5. This would allow sufficient precipitation of the additive elements. At the completion of the co-precipitation process, the obtained slurry was dried and calcined at 750 °C for 2 h under air to yield the final Y^{3+} and Fe^{3+} co-doped BZT powders.

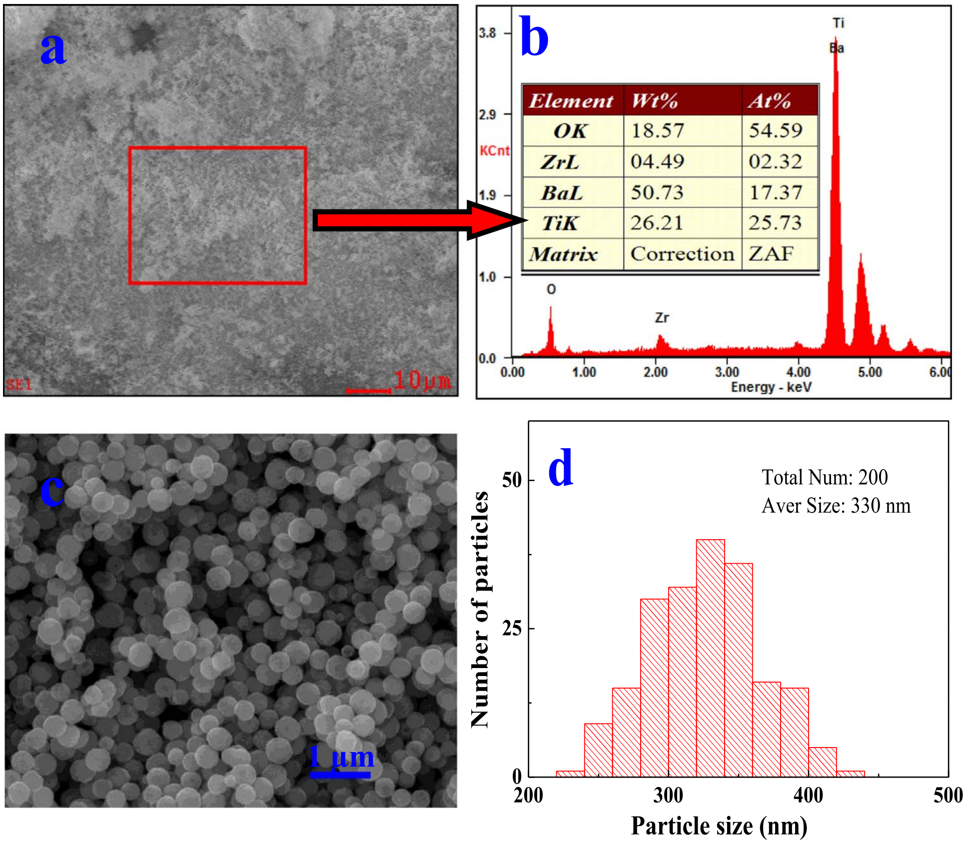
The finally obtained Y^{3+} and Fe^{3+} co-doped BZT powders were pressed into pellets (8 mm in diameter and 4 mm in thickness) using 6 MPa pressure induced by an uniaxial pressing equipment. The pellets were then sintered in air at 1160 °C for 2 h. The resulting BZT doped with Y^{3+} and Fe^{3+} ceramics at different concentrations of 0.02, 0.04, 0.06, 0.08 and 0.10 mol were denoted as BZTYF-1, BZTYF-2, BZTYF-3, BZTYF-4 and BZTYF-5, respectively.

The phase structure of the powders and ceramics were determined by X-Ray diffraction (XRD, D8 Advance; Bruker, Frankfurt, Germany) in the 2θ range of 20–70°. The morphology and microscopic structure of the samples were characterized by scanning electron microscopy (SEM, FEI, Quanta-600) and transmission electron microscopy (TEM, FEI, Tecnai G2 F20 S-TWIN) equipped with an energy-dispersive X-ray spectrum (EDX). The average size of $BaTiO_3$-based particles was calculated from $BaTiO_3$-based scanning electron images using a Nano Measurer software. The dielectric properties of the samples were estimated using an HP 4284A LCR meter (Hewlett-Packard, Palo Alto, CA, USA) controlled by a computer. The data were collected in the frequency range from 10^3 and 10^6 Hz and controlled testing temperatures from −60 °C to 150 °C at high and low gimbals.

3. Results and discussion

Fig. 1 shows the SEM (a) micrograph and EDS (b) data of the resulting $BaZr_{0.13}Ti_{1.46}O_3$ particles. The EDS of the selected area is depicted in Fig. 1a. Fig. 1b revealed the presence of all the additive elements (Ba, Zr, Ti and O), and their compositions measured by EDS were consistent with target compositions. These data also confirmed the ratio (0.13: 1.46) of (Zr^{4+}: Ti^{4+}) in $BaZr_{0.13}Ti_{1.46}O_3$ particles. Figs. 1c and 1d illustrate the morphology and size distribution of BZT particles obtained by the SEM measurements. The BZT particles appeared spherical in shape, with average grain size of around 330 nm.

The TEM images of BZT and BZTYF-5 particles are depicted in Fig. 2. Monodisperse submicron BZT particles with uniform morphologies could clearly be observed in Fig. 2a. The combination of these data with those of Fig. 1c and d suggested the narrower size distribution of the particles. Fig. 2(b–d) gathers the TEM images and EDS spectrum of BZTYF-5 particles. A uniform morphology and narrowed size distribution of the particles could clearly be noticed (Fig. 2b). The latter is important because an excellent dispersion of BZT particles is



Element	Wt%	At%
OK	18.57	54.59
ZrL	04.49	02.32
BaL	50.73	17.37
TiK	26.21	25.73
Matrix	Correction	ZAF

Fig. 1. SEM micrograph (a) and EDS (b) of $BaZr_{0.13}Ti_{1.46}O_3$ particles (EDS data of the selected area in a). FE-SEM images and grain-size distributions (c,d) of $BaZr_{0.13}Ti_{1.46}O_3$.