Preparation of $BaZr_xTi_{1−x}O_3$ by the hydrothermal process from peroxo-precursors

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Abstract

Crystalline $BaZr_xTi_{1−x}O_3$ (BZT) powders were synthesized through a hydrothermal reaction by using amorphous $BaZr_xTi_{1−x}$-peroxo-hydroxide. $BaZr_xTi_{1−x}$-peroxo-hydroxide precursors were prepared by coprecipitatation of $BaCl_2$, $ZrOCl_2$, $TiOCl_2$ and H_2O_2 aqueous solution added to ammonium solution. Additional $Ba(OH)_2$ was used as a mineralizer. This processing method provided a simple low temperature route for producing BZT fine powders, which could also be extended to other systems. It was found that phase-pure BZT powders with a cubic perovskite structure were synthesized under mild hydrothermal conditions (100–130 °C, ≤1.5 MPa). Ultra-fine BZT powders having the BET surface area of $30\,m^2/g$ were formed. The BZT ceramics sintered at a temperature as low as 1150 °C for 1 h had 93% of theoretical density. The higher Zr content leaded to a higher dielectric constant at room temperature and a more diffuse ferroelectic-to-paraelectric transition, which resulted in a reduced temperature dependency of the dielectric constant for the $BaZr_{0.2}Ti_{0.8}O_3$ ceramic.
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1. Introduction

Barium titanate ($BaTiO_3$) has superior dielectric properties and is used extensively in electronic components. For capacitor applications, especially in the form of multilayer ceramic capacitors (MLCC), the compositional and microstructure modification play an important role to meet the required dielectric constant and dielectric temperature characteristic. In particular, compositionally modified $BaZr_xTi_{1−x}O_3$ (BZT) received much attention due to the tunable structural and electrical properties to specific applications by the replacement of Ti^{4+} by Zr^{4+}.[1–3]

The hydrothermal synthesis route has the most potential for barium titanate-based ceramic powers due to the synthesis of homogeneous, ultra-fine and less contaminated powders at low synthesis temperatures.[2,4–6] Although the process offers a promising approach to prepare ultra-fine, crystalline ceramics by using an aqueous medium, the process has been conducted under strong alkaline conditions (>pH 13) with use of NaOH and/or KOH,[2,4–6] thus might be leaving the contaminants, Na^+ and K^+ cations. Alkaline cations (Na^+ or K^+) are known to be difficult to remove, influence the performances of the prepared powders and resulting sintered ceramics, and deteriorate the electrical properties of the ceramics.[7,8] Furthermore, in the conventional hydrothermal synthesis, crystallized powders are formed by dissolution of precursors (e.g. metal-hydroxides or -oxides) and precipitation (crystallization) process under the strong alkaline conditions. Therefore, for multi component system, each component is apt to have different dissolution or precipitation rate, which makes it difficult to control the exact composition of the final hydrothermal product.

The objective of the present work, was to examine the possibility of directly synthesizing BZT powder using peroxo-precursor in alkali-free system. A coprecipitated peroxo-hydroxide was used as a starting material in the hydrothermal reaction. $Ba(OH)_2$ was used as a mineralizer in alkali-free system. Compared with conventional hydrothermal synthesis, the present study offers the mild hydrothermal synthesis

conditions: fast and low-temperature synthesis under relatively low pH, as well as the convenient compositional control for the complex solid solution of $BaZr_xTi_{1-x}O_3$.

2. Experimental procedure

A chemically modified, amorphous peroxo-hydroxide precursor via coprecipitation was used to synthesize compositionally modified BZT ($BaZr_xTi_{1-x}O_3$, $x = 0$, 0.1 and 0.2) powders in hydrothermal conditions. A peroxo-complex solution of $BaZr_xTi_{1-x}$ was prepared by adding hydrogen peroxide (H_2O_2) in $BaCl_2$, $ZrOCl_2$ and $TiCl_4$ mixed aqueous solution. The $Ba/(Zr_xTi_{1-x})$ and $H_2O_2/(Zr_xTi_{1-x})$ molar ratios were fixed at 1 and 6, respectively. Amorphous $BaZr_xTi_{1-x}$-peroxo-hydroxide precipitate was formed by adding the peroxo-complex solution of $BaZr_xTi_{1-x}$ in an ammonium solution. The final pH of the solution was maintained at 12. The coprecipitated precursor was used as the starting material for the hydrothermal synthesis.

In hydrothermal synthesis, the suspension including coprecipitated precursor was charged into a teflon-lined autoclave of 300 ml capacity with a fill factor of 80 vol.% in the presence of $Ba(OH)_2$. The $Ba(OH)_2$ was used as a mineralizer. The $Ba(OH)_2$/BZT molar ratio was fixed at 2. The resulting pH in the aqueous solution obtained by addition of $Ba(OH)_2$ was 12.8. Subsequently, the reactor was heated to temperatures between 100 and 130 °C for various reaction times with autogeneous pressure. Maximum autogeneous pressure was ~1.5 MPa at 130 °C. The reaction products were filtered and washed with distilled water to remove soluble components, including excess Ba^{2+} and Cl^- and then dried at 90 °C for 12 h. The hydrothemally synthesized powders were pressed in the form of discs under a pressure of 80 MPa and sintered at 1150 °C for 1 h.

The properties of the prepared powders were characterized by thermo-gravimetric and differential thermal analysis (TG-DTA), X-ray powder diffractometry (XRD, Cu Kα) and scanning electron microscopy (SEM). The surface area of the powders was measured by the BET technique. The dielectric constant for the sintered ceramics was measured by an inductance, capacitance, and resistance (LCR) meter at 1 kHz.

3. Results and discussion

3.1. Coprecipitation of peroxo-hydroxide precursor

In an aqueous solution, the basic principle of coprecipitation is a solubility change of metal-hydroxides depending on pH. It is well known that the peroxide routes can produce the homogeneous precipitates below pH 12 with NH_4OH[9,10] for both titanates and zirconates. The peroxide route for homogenous coprecipitation can be extended to $BaZr_xTi_{1-x}$-peroxohydroxide system. The formation of the coprecipitates can be
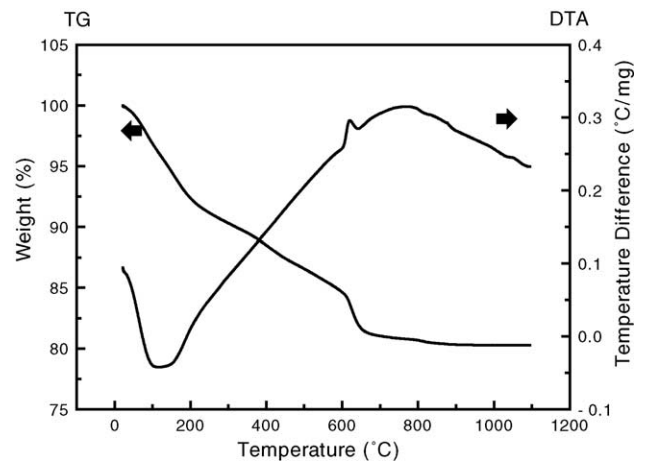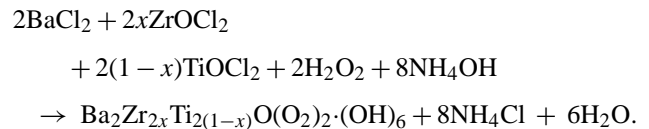

Fig. 1. TG-DTA curves of BZT ($BaZr_{0.2}Ti_{0.8}O_3$) powders prepared by coprecipitation.

described by the following reaction:

$$2BaCl_2 + 2xZrOCl_2$$
$$+ 2(1-x)TiOCl_2 + 2H_2O_2 + 8NH_4OH$$
$$\rightarrow Ba_2Zr_{2x}Ti_{2(1-x)}O(O_2)_2 \cdot (OH)_6 + 8NH_4Cl + 6H_2O.$$

TG-DTA analysis of $BaZr_{0.2}Ti_{0.8}O_3$ powders prepared by the coprecipitation is presented in Fig. 1. For the coprecipitates, the reaction involving a considerable amount of weight loss (~20%) resulting from decomposition of hydroxide was finished at around 600 °C. The exothermic peak at around 600 °C was due to the transition from amorphous to perovskite. The TG-DTA results for the $BaZr_{0.2}Ti_{0.8}O_3$ powders were identical, as were the results obtained by XRD patterns (Fig. 2) of heat-treated powders at different temperatures. As-prepared powder was amorphous and transformed into the perovskite without intermediate impurity phase at 600 °C. Although the synthesis temperature was substantially lower than those (900–1100 °C) of the conventional solid state reaction process, the coprecipitation needed a calcination step
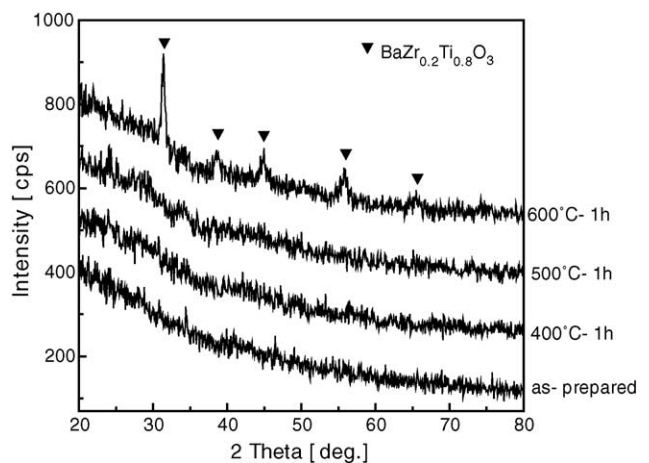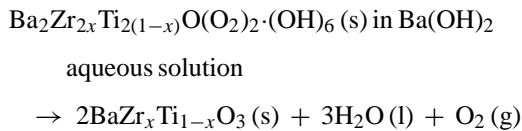

Fig. 2. XRD patterns of the coprecipitated BZT ($BaZr_{0.2}Ti_{0.8}O_3$) powders heat-treated at different temperatures.

at relatively high temperature and also require a consequent milling process.

3.2. Hydrothermal synthesis

Fig. 3 shows XRD patterns of as-prepared powders and sintered ceramics derived from hydrothermal synthesis at different synthesis conditions. Well-developed BZT-perovskite without impurity phase was formed. Hydrothermal transition from the amorphous peroxo-precursors to crystalline perovskite instantaneously happens at temperature as low as 100 °C, without holding time as shown in Fig. 3a. When the reaction conditions reach certain synthesis conditions, the transition from the $Ba_2Zr_{2x}Ti_{2(1-x)}O(O_2)_2 \cdot (OH)_6$ precursor to the $BaZr_xTi_{1-x}O_3$ powder takes place via the following reaction:

$Ba_2Zr_{2x}Ti_{2(1-x)}O(O_2)_2 \cdot (OH)_6$ (s) in $Ba(OH)_2$

    aqueous solution

    $\rightarrow 2BaZr_xTi_{1-x}O_3$ (s) $+ 3H_2O$ (l) $+ O_2$ (g)

The improved compositional homogeneity of coprecipiated $Ba_2Zr_{2x}Ti_{2(1-x)}O(O_2)_2 \cdot (OH)_6$ precursor via the peroxide route were supposed to provide lower phase transition barrier and offered the mild hydrothermal synthesis conditions such as lower reaction temperatures and lower pH.

A typical TG-DTA result for the hydrothermally prepared $BaZr_{0.2}Ti_{0.8}O_3$ powders is presented in Fig. 4. The total weight between 90 °C and 1100 °C is <5 wt.% for the powders. The total weight loss consists of three contributions: the first region (<250 °C) corresponds to the loss of physically adsorbed water, the second region between 250 and 600 °C corresponds to the loss of chemically bound hydroxyl groups which was defectively incorporated in the perovskite lattice[4] and finally, the slight weight loss above 800 °C is due to CO_2 release from decomposition of carbonate species.[4,5]

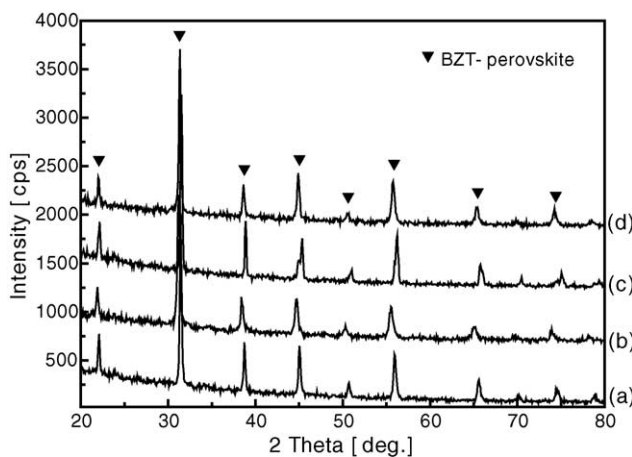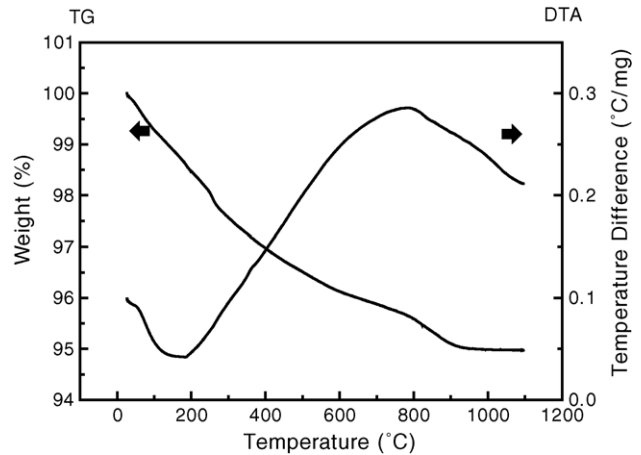Fig. 4. TG-DTA curves of BZT ($BaZr_{0.2}Ti_{0.8}O_3$) powders prepared by hydrothermal process conducted at 130 °C for 1 h.

Fig. 5 shows the SEM morphology of the synthesized $BaZr_{0.2}Ti_{0.8}O_3$ powders prepared at 130 °C for 1 h. It can be easily seen from SEM photomicrographs that the synthesized BZT powder consists of ultra-fine particulates. The value of specific surface area (S_{BET}) of the as-prepared powders determined by BET analysis was an average value of 30 m^2/g. The particle size ($D_{BET} = 6/\rho S_{BET}$, where ρ is the theoretical density of the powder) calculated from the value of specific surface area was ~35 nm. With use of the reactive fine powders prepared by the hydrothermal synthesis in this study, a high density of 93% of theoretical was obtained for the ceramics sintered at a temperature as low as 1150 °C for 1 h.

The average values of dielectric constant of the BZT ceramics with $x = 0$, 0.1 and 0.2 were 1700, 2200 and 3500 at room temperature, respectively. Fig. 6 shows the temperature dependence of the dielectric constant of BZT ($x = 0$ and 0.2)
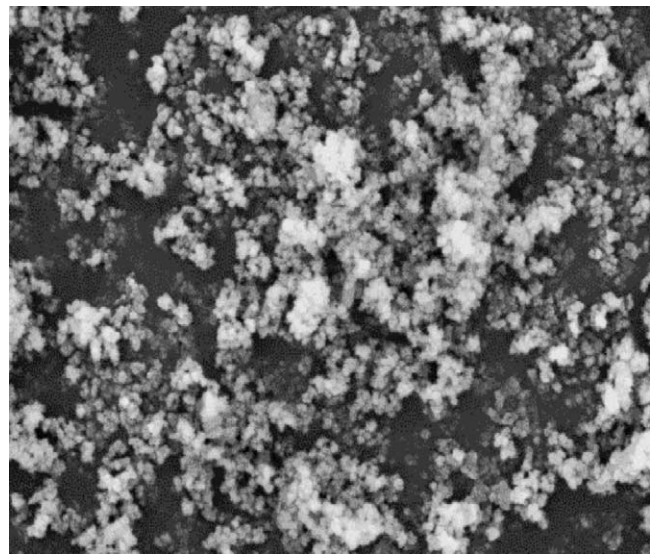

Fig. 3. XRD patterns of hydrothermal BZT powders: (a) $BaTiO_3$ prepared at 100 °C without holding time; (b) $BaZr_{0.2}Ti_{0.8}O_3$ prepared at 130 °C for 1 h and ceramics; (c) $BaTiO_3$ from powder (a); and (d) $BaZr_{0.2}Ti_{0.8}O_3$ from powder (b), sintered at 1150 °C for 1 h.

Fig. 5. SEM micrograph of BZT ($BaZr_{0.2}Ti_{0.8}O_3$) powders hydrothermally prepared at 130 °C for 1 h.
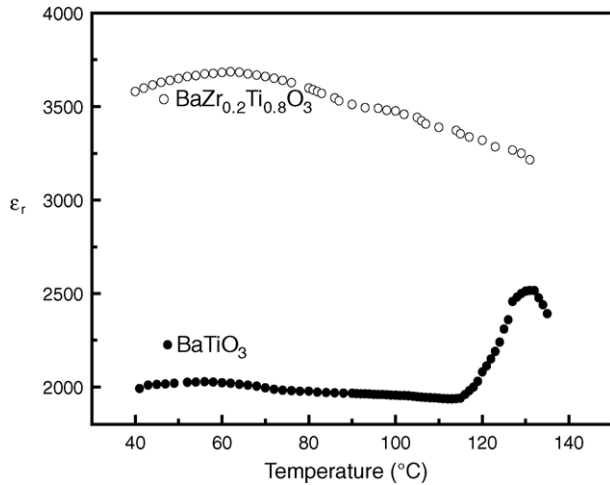
Fig. 6. Dielectric constant of BZT ceramics as a function of temperature.

ceramics sintered at $1150\,^{\circ}\mathrm{C}$ for 1 h. For the $BaZr_{0.2}Ti_{0.8}O_3$ ceramics, it was shown that the more diffuse ferroelectic-to-paraelectric transition and the reduced temperature dependency ($<20\%$) of the dielectric constant between room temperature and $130\,^{\circ}\mathrm{C}$ were obtained.

4. Conclusions

The modified hydrothermal approach using the $BaZr_xTi_{1-x}$-peroxo-hydroxide precursor and additional $Ba(OH)_2$ used as a mineralizer offered a simple low temperature route for producing crystalline BZT fine powders. The compositional homogeneity of coprecipiated $Ba_2Zr_{2x}Ti_{2(1-x)}O(O_2)_2\cdot(OH)_6$ precursor provided lower phase transition barrier and caused the mild powder synthesis conditions over the conventional hydrothermal process.

The prepared powder consists of nano-sized crystallites with BET surface area as high as $30\,\mathrm{m^2/g}$. The resulting powders offered low ceramic processing temperatures and high-density ceramic products. In BZT ceramics, the higher Zr content leaded to the higher dielectric constant at room temperature, the more diffuse ferroelectic-to-paraelectric transition and the smaller temperature dependency of the dielectric constant.

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