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Letter

Sinterability and nonlinear dielectric properties of $Ba_{0.6}Sr_{0.4}TiO_3$ derived from a citrate method

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ABSTRACT

$Ba_{0.6}Sr_{0.4}TiO_3$ powder was prepared by a citrate precursor method, and the sinterability and nonlinear dielectric properties of the resulting specimens were investigated. Superfine powder with a pure perovskite phase was produced at a relatively low calcining temperature of 650 °C by carefully controlling the synthesis process. Adopting the superfine powder was found to be effective in reducing sintering temperature and forming a fine-grained microstructure, which in turn contributed to reducing the dielectric loss and enhancing the figure of merit (FOM). At room temperature, the ceramic specimen sintered at 1250 °C attained a dielectric loss of 0.22% at 10 kHz and a FOM of 142 at 10 kHz and 20 kV/cm. Moreover, a remarkable contribution of polar micro-regions to the nonlinear dielectric behavior was revealed for the ceramic specimen. This phenomenon was qualitatively interpreted with respect to the dielectric responses of the micro-regions under bias electric fields of different magnitudes.

1. Introduction

In the past decades, barium strontium titanate ($Ba_{1-x}Sr_xTiO_3$, BST) has drawn increasing research interest because of its strong dielectric nonlinearity under bias electric field and linearly adjustable Curie temperature with the strontium content over a wide temperature range. The desired properties make BST a promising candidate material for tunable microwave dielectric devices [1]. The applications of BST in tunable microwave devices have been explored in various forms, such as bulk ceramics, thin films and thick films [2]. BST thick films exhibit the merits of lower fabrication costs compared with the thin films and smaller bias voltages required for tuning relative to the bulk ceramics. Fabricating BST thick films on alumina substrates by screen-printing or tape-casting has been believed to be cost-effective and flexible in view of mass production [3,4]. However, these thick films suffer from severe reactions with the substrates at high sintering temperatures [3,5]. Therefore, their sintering temperatures have to be limited to less than 1300 °C, which, in turn, leads to porous thick films with poor adhesion to the substrates [5].

Adding sintering aids, such as glass frits [5,6] and oxide additives [3,7], is an usually employed strategy to overcome the problem. Nevertheless, the reactions between BST thick films and the sintering aids may result in unfavorable changes in the structure and dielectric properties [6]. Thus, improving the sinterability of BST materials without adding sintering aids appears as an intriguing subject of practical importance. Adopting superfine starting powders with high reactivity is a viable approach to enhance the sinterability of BST materials. There have been extensive researches on preparing superfine BST powders by various chemical solution methods, such as hydrothermal synthesis [8,9], sol–gel process [10], co-precipitation route [11] and citrate precursor method [12,13]. The citrate method is essentially a polymeric precursor method, using citric acid and water as the complex agent and solvent, respectively. Our previous researches have demonstrated the advantages of the citrate method in producing perovskite-type complex oxide systems in terms of desired powder morphology, improved sinterability and enhanced electric properties [14,15]. So far as we know, there are few reports on the sinterability and nonlinear dielectric properties of BST materials derived from the citrate method. A research effort on this topic is thus warranted.

As has been well recognized, BST compositions with a paraelectric state at application temperatures are preferred from the viewpoint of developing tunable microwave devices because of a good property combination including relatively high dielectric nonlinearity and relatively low dielectric loss [2]. Therefore, we prepared $Ba_{0.6}Sr_{0.4}TiO_3$ ceramics by the citrate method. In this work, we report the preliminary results with respect to synthesis process control, sinterability and nonlinear dielectric properties.

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2. Experimental

The powder with the nominal composition of $Ba_{0.6}Sr_{0.4}TiO_3$ was synthesized by the citrate method. Reagent grade $Ba(NiO_3)_2$, $Sr(NiO_3)_2$, tetrabutyl titanate and citric acid were used as starting materials. A weighed amount of citric acid was dissolved into deionized water in a beaker. An appreciate amount of aqueous ammonia was dripped to adjust the pH value of the solution to 7–9. A designed amount of tetrabutyl titanate was slowly added under a stirring at 70 °C to form a transparent aqueous solution. Various nitrates were then added according to the nominal composition. The mole ratio of citric acid to the total metal cation content was 1.25. After stirring at 80 °C for 1 h, a transparent precursor solution with a pH value of about 6 was yielded. The precursor solution was subjected to heating in an oven at 200 °C to form a foam-like solid precursor. The foam precursor was pulverized and calcined at 550–700 °C for 1 h in air. The calcined powders were uniaxially pressed under a pressure of 300 MPa into discs of 19 mm in diameter and 1 mm in thickness. The compacted discs were subsequently sintered at 1250 °C for 2 h in air.

Thermogravimetry (TG) and differential scanning calorimetry (DSC) analyses of the foam precursor were performed by a Netzsch STA 449C simultaneous thermal analyzer at a heating rate of 5 °C/min in air. The phase purity of the calcined powders and crystal structure of the ceramic specimens were examined by a Philips X'pert PBO X-ray diffractometer using Cu K_α radiation. The morphology of the calcined powders was observed at a Jeol JSM-5610LV scanning electron microscope (SEM) and a Hitachi S-4700 field emission scanning electron microscope (FESEM), respectively. The microstructure of the ceramic specimens was investigated at the SEM apparatus using thermally-etched surfaces. The dilatometric measurement of the compacted powder was conducted by a Netzsch DIL 402C dilatometer at a heating rate of 5 °C/min between 20 and 1300 °C in air. The density of the ceramic specimens was measured by the Archimedes method with ethyl alcohol as the medium. The ceramic specimens were painted with silver paste on both surfaces as electrodes. The temperature dependence of the dielectric constant (ε_r) was measured by a HP4294 impedance analyzer and a JYT-800L environmental chamber between −60 and 120 °C at 0.1, 1, 10 and 100 kHz, respectively. The polarization–electric field (P–E) relation was measured at room temperature by a Radiant precision workstation based on a Sawyer-Tower circuit at 50 Hz. The nonlinear dielectric properties were measured at room temperature by a TH2818 impedance meter at 10 kHz under external bias electric fields rising from 0 to 20 kV/cm.

3. Results and discussion

Fig. 1 shows the TG–DSC curves of the foam precursor. One can see a tiny weight loss of 1.7% around 100 °C. It is ascribed to the evaporation of adsorbed water. There are two successive exothermic peaks in the range of 300–600 °C, an obscure one near 350 °C and an evident one around 460 °C, corresponding to a total weight loss of 42.3%. It is assigned to the thermal decomposition of the foam precursor. A faint exothermic peak occurred at 610 °C, accompanied by a small weight loss of 3.1%. This is considered to be caused by the decomposition of residual oxycarbonate of barium and strontium [13]. No further DSC peak or weight loss can be seen thereafter.

Fig. 2 shows the X-ray diffraction (XRD) patterns of the powders calcined at different temperatures. After calcining at 550 °C, a perovskite phase was detected together with a small amount of impurity phase. The impurity phase is assigned to the residual oxycarbonate [13]. A minor amount of the impurity phase was still distinguishable after calcining at 600 °C. Further increasing the calcining temperature to 650 and 700 °C, respectively, produced a pure perovskite phase. The phase development of the powder with increasing calcining temperature is basically consistent with the analysis of the TG–DSC curves in Fig. 1. The calcining temperature required for forming a pure perovskite phase (650 °C) is considerably reduced compared to those (1150–1200 °C) of the conventional solid-state reaction method [16]. This calcining temperature is also comparatively lower than previously reported results regarding synthesizing $Ba_{0.6}Sr_{0.4}TiO_3$ powders by the citrate method. It has been reported that (Ba, Sr)CO_3 impurity phase was detected in $Ba_{0.6}Sr_{0.4}TiO_3$ powders derived from the citrate method, with a calcining temperature of 800 °C being necessitated to eliminate the impurity phase and form a pure perovskite phase [12,13]. The comparatively lower calcining temperature in the present work is believed to be attributed to a careful control of the calcination process. We found that keeping slow heating rates (e.g. 1 °C/min) between 400 and 650 °C during the calcination is crucial in suppressing the formation of the (Ba, Sr)CO_3 impurity phase.

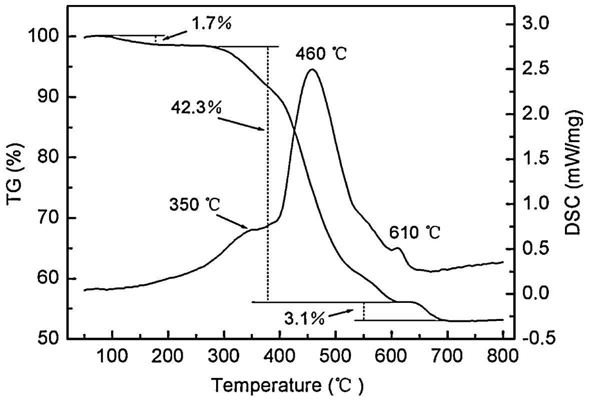

Fig. 1. TG–DSC curves of the foam precursor.

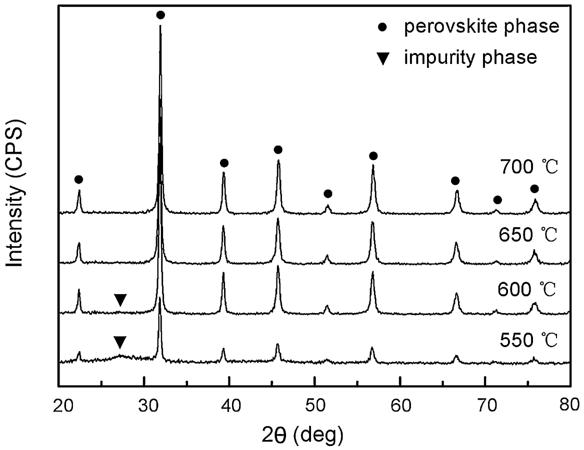

Fig. 2. XRD patterns of the powders calcined at different temperatures.

Fig. 3 shows the morphology of the powder calcined at 650 °C. As shown in Fig. 3a, the powder is consisted of homogeneous and fine particles. The FESEM micrograph (Fig. 3b) further reveals the particle morphology. One can see sphere-like primary particles around 40 nm and agglomerations composed of several primary particles. Considering the pure perovskite phase and fine morphology of the powder calcined at 650 °C, the specimens investigated in the following part were made from the powder unless otherwise mentioned.

Fig. 4 shows the dilatometric curves of the compacted powder. The dilatometric measurement indicated an onset temperature of shrinkage at around 1060 °C and a fast shrinkage increment with increasing temperature up to 1300 °C, with a maximum shrinkage rate appearing at 1220 °C. The onset temperatures of shrinkage for $Ba_{0.6}Sr_{0.4}TiO_3$ powders prepared by the conventional method have been reported to be located at higher temperatures (1200–1250 °C) [16]. Correspondingly, their sintering temperatures are usually between 1350 and 1450 °C [3,16,17]. The shrinkage behavior in Fig. 4 hints a relatively lower sintering temperature for the powder prepared by the citrate method. As expected, the ceramic specimen sintered at 1250 °C showed a relative density of 95.5% and a radial shrinkage of 20.5%. The relative density is comparable with those of $Ba_{0.6}Sr_{0.4}TiO_3$ ceramics prepared by the conventional method and sintered at 1400 °C or higher temperatures [3,16,17]. This value is also competitive to that of $Ba_{0.6}Sr_{0.4}TiO_3$ ceramic added with 0.5 wt.% B_2O_3 as sintering aid and prepared by the conventional method by sintering at 1250 °C [3]. Fig. 5 shows the SEM micrograph of the ceramic specimen. One can see a dense microstructure with generally uniform and fine grains of about 1 μm. These results