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Fabrication and influence of sintering temperature on material properties of Mn/Y codoped $Ba_{0.67}Sr_{0.33}TiO_3$ ceramics via using citrate–nitrate combustion derived powder

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ABSTRACT

Mn/Y codoped $Ba_{0.67}Sr_{0.33}TiO_3$ (BST) ceramics were fabricated via using citrate–nitrate combustion derived powder, and the effect of sintering temperature on microstructure and electrical properties of BST ceramics were mainly investigated. Agglomerated BST powder, with nano-size particles, was obtained at 700 °C. Sintering temperature has a strong influence on the microstructure and electrical properties of BST ceramics. The density, dielectric and ferroelectric properties are improved by optimizing sintering temperature. The relative density of the BST ceramics sintered at an optimum sintering temperature (1260 °C) reaches 97.9% of the theoretical value. The measured values of remanent polarization ($2Pr$) and coercive field ($2Ec$) of the BST ceramics are 16.33 μC/cm^2 and 3.548 kV/cm, respectively. The dielectric loss of the BST ceramics is 0.003 in the para-electric state. Therefore, nanocrystalline powder, sintering with optimum temperature and Mn/Y codoping help improve the electrical properties of BST ceramics.

1. Introduction

Over the last decade, much attention has been given to the development of pyroelectric materials for heat–electric conversion in infrared detector and thermal imaging [1–4]. $Ba_{1-x}Sr_xTiO_3$ ceramics have been considered as a promising candidate for such applications due to a noticeable change in the dielectric constant with a paraelectric-to-ferroelectric phase transition taking place, which allows a large pyroelectric coefficient to be obtained in the vicinity of phase transformation temperature [5]. And the temperature at which the material displays its largest temperature sensitivity can be matched exactly to devices' ambient temperature simply by changing Ba/Sr ratio [6], which enables the devices for use close at room temperature. The major challenge in designing material systems for pyroelectric devices is the simultaneous requirement of a high pyroelectric coefficient, a low heat capacity, and low dielectric constant and loss [7]. Since material properties are strongly related to the microstructure of materials, fabricating homogeneous and uniform materials is important. Low-temperature synthesis of nanoscaled $Ba_{1-x}Sr_xTiO_3$ powders has attracted considerable interest in recent years due to the technological importance of these powders in the fabrication of high-quality ceramics. As reported, the powders can be synthesized via a lot of chemical methods such as coprecipitation [8] and hydrothermal [9–12]. Stoichiometric deviation is the most crucial problem existing in the two methods. Recently, the citrate gel method which is based on the Pechini-type route [12] has been widely used to prepare the powders [13,14]. However, to the best of our knowledge, this method involves too complex processes, and the powders obtained were always badly agglomerated.

The codoping is an effective way to optimize the electrical properties of $Ba_{1-x}Sr_xTiO_3$ ceramics [14], improving the ferroelectric properties and reducing the leakage current. For example, Mn/Y codoped BST capacitors exhibit improved ferroelectric properties and lower dielectric loss ($\tan\delta < 0.0073$ at 1 kHz). Therefore, the introduction of namocrystalline synthesis combined with Mn/Ycodoping presents an intriguing opportunity to develop BST material for pyroelectric device applications with stringent demands focused on low dielectric loss and leakage current, while still maintaining a moderate pyroelectric coefficient. In this work, we present a simple citrate–nitrate combustion method for the synthesis of nanocrystalline BST powder and study the effect of sintering temperature (Ts) on the bulk density, microstructure, and electric properties of BST ceramics, confirming nanocrystalline powder, sintering with an optimum temperature, and Mn/Y codoping help improve the electrical properties of BST material.

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2. Experimental procedure

The citrate–nitrate combustion (CNC) method was used to synthesize Mn/Y codoped BST nanopowder following the composition of $Ba_{0.67}Sr_{0.33}TiO_3$ codoped with 0.5 mol% for Mn and 1.0 mol% for Y dopants. Required amounts of barium nitrate, strontium nitrate, tetraethyl titanate solution and additions were dissolved in citrate solution to prepare the precursor solution with the desired stoichiometry for the BST, which Manganese acetate and yttrium oxide were used as a source of Mn and Y, and glacial acetic acid and glycol were used as the solvents of tetrabutyl-titanate. And the pH value of the solution was adjusted to 6–7 with ammonia water in order to the ionization of citrate. Then the precursor solution was placed in a furnace and dried at 150 °C for 24 h to dehydrate, condense, promote polymerization, break organic bonds and transform into soft and porous black precursor powder. Finally, the powder was calcined at 800 °C for 2 h to synthesize the BST powder, and the BST powder obtained were crushed to fine powder, pressed uniaxially into pellets, and sintered into ceramics at different temperatures between 1020 and 1340 °C for 3 h.

Thermogravimetry (TG) and differential scanning calorimetry (DSC) analysis of the precursor powder were performed by a Netzsch STA 449C simultaneous thermal analyzer at a heating rate of 10 °C/min in air. The crystal structure and surface morphology of BST ceramics were determined via X-ray diffraction (XRD) and scanning electron microscope (SEM). The temperature dependence of dielectric properties was determined using a temperature measurement apparatus and a temperature control box attached to an Agilent E4980A LCR meter. The polarization electric-field (*P*–*E*) hysteresis loops were measured using Radiant Precision Ferroelectric Measurement System (RT2000 Tester, USA).

3. Results and discussion

In order to understand the synthesis process for BST, and to determine synthesis temperature of BST powder, the black precursor powder was characterized by TG/DSC analysis, and the powders calcined at different temperatures from 500 °C to 900 °C for 2 h were examined using XRD analysis.

Fig. 1 shows the XRD patterns of the calcined powders. It is observed that the powder calcined at 500 °C mostly shows amorphous nature together with a small amount of $(Ba,Sr)_2Ti_2O_5CO_3$ and $(Ba,Sr)CO_3$. Heat treatment with appropriate temperature can cause the amorphous phase to crystallize because the amorphous phase is a thermodynamically metastable state. This is what we observed, when calcination temperature was raised from 500 °C to 600 °C. At 600 °C, the powder is well transformed to a crystalline state, simultaneously, $(Ba,Sr)_2Ti_2O_5CO_3$ disappeares and only a smaller amount of $(Ba,Sr)CO_3$ exists. The BST peaks observed for the powder calcined at 700 °C are sharp, and $(Ba,Sr)CO_3$ peak disappeares, revealing that a pure BST phase was obtained.

The TG/DSC plots of the black precursor powder, heated from ambient temperature to 1000 °C, are shown in Fig. 2. The TG trace indicates there are decreases in the powder weight over the temperature ranges of 35–112 °C, 112–618 °C, and 618–670 °C. During the first step, the weight loss was close to 4.33%, which could be attributed to the removal of water from the precursor. An endothermic peak near 78.6 °C is found in the DSC curve. The second step with a weight loss of 69.48% was recorded for the decomposition of the citrate precursor, the formation of intermediate products, and the nucleation and crystallization of the BST. This process consists of two stages, which can be inferred from the position of the endothermic and exothermic peaks in the DSC curve. In the first stage from 112 to 238 °C, the endothermic peak at 184 °C is attributed to the decomposition or removal of the organic parts which combined weakly with others in the citrate precursor. On the other hand, there are three exothermic peaks around 292.9 °C, 483.8 °C, and 615.2 °C, corresponding to the drastic combustion of the organic species involved in the precursor powder, the formation of BST phase via a solid state reaction between nanocrystalline $(Ba,Sr)CO_3$ and amorphous TiO_2, and its crystallization. During the last step, there were a weight loss of 1.65%, and a broad endothermic peak at 641.6 °C, corresponding to the crystallization of BST via solid-state reaction between residual carbonates and amorphous TiO_2. This can be confirmed by the XRD analysis (Fig. 1).

The morphology of BST powder was investigated by SEM. Fig. 3 shows the SEM image of the powder obtained at 800 °C. Most of the calcined powder is agglomerated, and its shape is not uniform. To determine the average particle size of the powder, measurements were taken along the length and width of several particles and the average of these measurements were calculated. The average particle size of the powder was found to be less than 100 nm.

The Archimedean method was used for bulk density measurements of BST ceramics. Relative densities were calculated as percentages of measured density compared to theoretical density. The bulk and relative densities of BST ceramics, sintered at different temperatures from 1020 °C to 1340 °C, are shown in Fig. 4. The density of BST ceramics, firstly, sharply increases from ~4.28 (g/cm^3) to ~5.34 (g/cm^3), reaches a maximum value of ~5.62 (g/cm^3) with increasing the sintering temperature from 1020 °C to 1260 °C, and then remains unchanged with further increasing the sintering temperature. As a result, the optimum sintering temperature is 1260 °C, in which the bulk density value of BST ceramics reaches 5.62 (g/cm^3), the relative density value 97.9% and the shrinkage 15.78%, and helps to enhance the density of BST ceramics.

Fig. 5 plots the XRD patterns of BST ceramics sintered at different temperatures. These XRD patterns reveal that all ceramics are a pure polycrystalline perovskite structure, indicating that the additions of Mn and Y are dissolved in the BST perovskite lattice. No remarkable difference in the XRD patterns was detected among

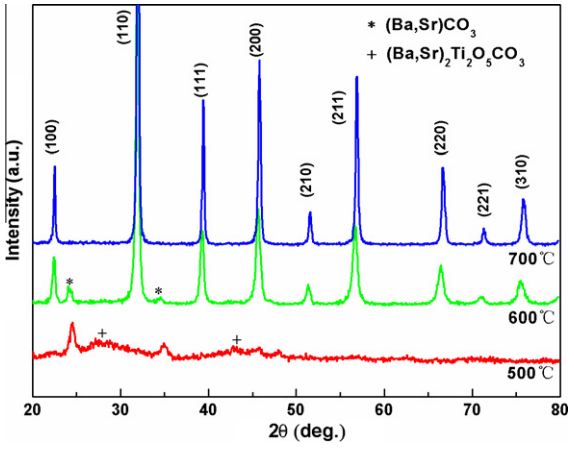

Fig. 1. XRD patterns of Mn/Y codoped BST powders calcined at different temperatures for 2 h.

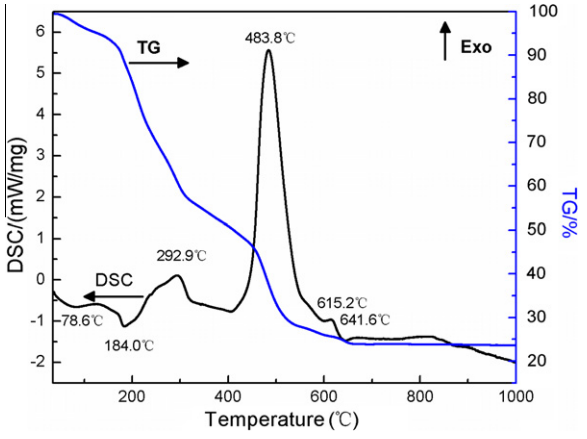

Fig. 2. DSC–TG curves of the precursor in air with a heating rate of 10 °C min^{-1}.