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A novel method for preparation of barium strontium titanate nanopowders

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ABSTRACT

$Ba_{0.6}Sr_{0.4}TiO_3$ (BST) nanopowders have been prepared using the modified citrate method with ammonium nitrate as a combustion promoter, and the formation mechanism, phase evolution, and particle size have been investigated using TG/DTA, XRD, and SEM. It is found that the peaks of barium carbonate disappear when the precursor powders are calcined at 650 °C. The fine particles of the nanopowders calcined with the combustion promoter addition are homogeneous and well-dispersed and their narrow size distribution is about 60–90 nm. Comparatively, the particles of the powder calcined without the ammonium nitrate addition are inhomogeneous, with an evident agglomeration. The mechanism for the above results is attributed to that a reaction can generate soft and loose precursor powders by the adoption of ammonium nitrate, and hence a pure BST phase could occur at the low synthesis temperature of 650 °C.

1. Introduction

As a ferroelectric material, barium strontium titanate (BST) possesses a high dielectric constant and a composition-dependant Curie temperature, and hence shows potential applications in piezoelectric and pyroelectric sensors, dynamic random access memories (DRAM), and microwave phase shifters [1–3]. To achieve the desired properties and practical applications, the quality of the BST powders are very important, which depends strongly on their synthesis. It is known that fine, homogeneous, and dispersive nano-sized powders are necessary for the development of uniform microstructure and desired properties. To this end, it is crucial to develop a simple and effective synthesis approach.

For the preparation for BST powders, the conventional solid-state reaction is used. The main operation is that barium carbonate, strontium carbonate and titanate oxide are calcined at high temperature around 1200 °C[4], which leads to many disadvantages such as large particle sizes, non-homogeneity and presence of impurities. So many studies have focused on various chemical methods for the synthesis of BST powders, for example, sol–gel, co-precipitation, hydrothermal and spray pyrolysis [5–8].

Conventional hydrothermal methods have been successfully used for the synthesis of BST powders [9]. In particular, the microwave hydrothermal synthesis can avoid high temperature heat treatment that can lead to the particle growth and agglomeration. However the use of large excess of barium and strontium precursors and low yield are two major drawbacks of the method. In addition, co-precipitation method for synthesis of BST powders has been reported, in which Barium strontium titanyl oxalate (BSTO) [$Ba_{1-x}Sr_xTiO(C_2O_4)_2$–$4H_2O$] are prepared firstly and then the BST powders are produced by the pyrolysis of BSTO at high temperature in air [10]. The route is simple and can produce stoichiometric, sub-micron-sized, almost unagglomerated BST powders. However, the process adds some unwanted ionic species and pH value is different in the steps. So the co-precipitation method suffers from two major problems, i.e., contamination of final precipitate with Cl^- ions and very stringent control of pH value.

Recently, the citrate method based on the chelating interaction between anion and metal ions has been proposed without the contamination of Cl^- and Na^+ ions [11]. More important, this method can remove other unnecessary ions. However, it is difficult to eliminate the carbonate phase and the temperature for a pure BST phase is too high (above 800 °C) [12], which causes particle growth and a reduction in surface area. These shortcomings also limit the wide applications of the citrate method.

In this work, a simple and effective method is developed for synthesis of BST nanopowders. The nanopowders are prepared at relatively low temperature 650 °C and show homogeneous, fine and well-dispersed characteristics with an average size about 60–90 nm.

2. Experiment

2.1. Synthesis

BST powders are synthesized by the citrate gel method as summarized in Fig. 1.

Barium nitrate, strontium nitrate, citrate and tetrabutyl titanate are used as raw materials. Firstly 0.3 mol citrate is dissolved into

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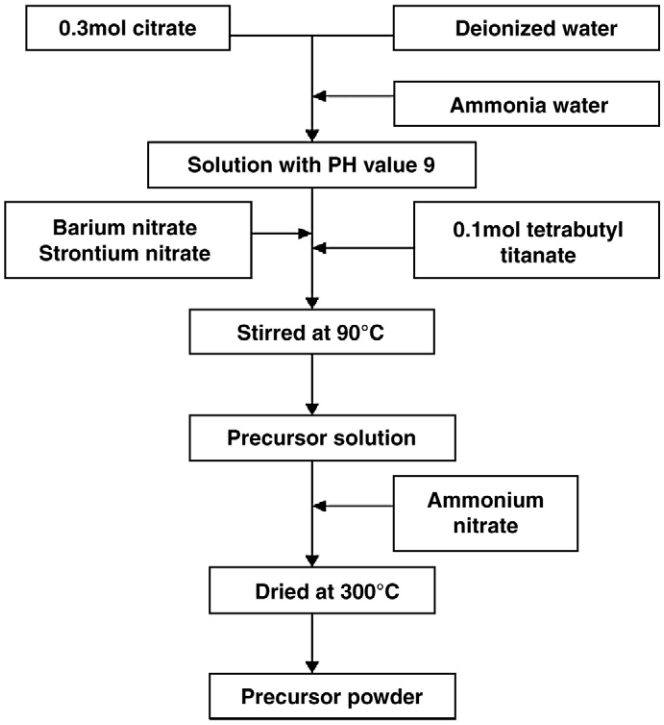

Fig. 1. Flowchart for preparing BST powders by citrate gel method.

100 ml deionized water. And the pH value of the solution is adjusted to 9 with ammonia water in order to the ionization of citrate. Then 0.1 mol tetrabutyl titanate is dropped into the above solution and stirred for 3 h at the temperature 90 °C until it became transparent and clear. Subsequently 0.06 mol barium nitrate and 0.04 mol strontium nitrate is added into the above solution respectively which is kept about 100 ml with adding deionized water. A bit of white precipitate is observed at first and disappears immediately and the solution is continuously stirred on a magnetic stirrer for about 3 h until it becomes transparent and yellow. The molar ratio of citrate acid and all metal ions is 1.5:1. The final solution is hereinafter referred to precursor solution.

The precursor solution is placed in a furnace and dries at 300 °C for 1 h to dehydrate, condense, promote polymerization and break organic bonds. Many reactions are accomplished at the same time in the process so that the synthesis of BST powders is simplified largely. The resulting products, i.e., soft and porous powders can be obtained. The powders are referred to precursor powders for BST. Finally white BST powders are obtained by heat treatment of the precursor powders at different temperatures in a muffle furnace.

2.2. Characterization

2.1.1. Thermal analysis

Thermogravimetric (TG) analysis and differential thermal analysis (DTA) of the gel are performed by a TAS-100 thermal analyzer (Rigaku Corporation, Japan). They are carried out under static air with a heating rate of 10 °C/min from room temperature to 1000 °C.

2.1.2. Structural characterization

The crystalline structure of the calcined powder is examined by a X-ray diffractometer. The X-ray diffraction data are obtained using a Rigaku RINT2000 diffractometer (42 kV × 120 mA) with CuKa radiation ($\lambda_{k\alpha1} = 1.5405^0A, \lambda_{k\alpha2} = 1.5443^0A, I_{k\alpha1}/I_{k\alpha2} = 0.5$), in the 2θ range between 10° and 80°, step 0.02° (2θ) with 6.0 s per point, using a divergence slit = 0.05 mm and receiving slit = 0.3 mm.

2.1.3. Morphological observation

The calcined powders are observed using a JSM-5610LV scanning electron microscope (SEM, Jeol Ltd., Japan). The microstructure and particle size of the produced BST powders can be obtained based on SEM images.

3. Result and discussion

In order to understand the synthesis process for BST, TG/DTG analysis is performed for the precursor powders and the results are shown in Fig. 2.

There is one faint endothermic peak at 90.4 °C, which corresponds to a small weight loss of 4.85% and is ascribed to the evaporation of absorbed water on the surface of the precursor powders. And one large and sharp exothermic peak at 450.2 °C, accompanied by a large weight loss of 38.08 %, is associated to the combustion of remaining organic components.

To evaluate the influence of temperature on the formation of carbonate and study the reaction mechanism the precursor powders are calcined at different temperatures. Fig. 3. shows the XRD patterns of the as-prepared and heat-treated powders.

It can be seen that the as-prepared powders are amorphous. The amorphous nature of the precursor powders exist below 500 °C. The perovskite BST crystallization has occurred during the heat treatment of the precursor in air at 500 °C accompanied by the faint peaks of barium carbonate. And the peaks of barium carbonate become weaker when the calcined temperature increased. As the temperature increases to 650 °C, peaks of barium carbonate disappeares and a pure BST phase is obtained. A solid state reaction may take place during the process, which is similar to the results reported by Mao [12].

$$(Ba, Sr)CO_3 + TiO_2 \rightarrow (Ba, Sr)TiO_3 + CO_2$$

However, compared with the results reported in these references [13,14], the calcined temperature which a pure phase is obtained is very low and the corresponding socking time is very short in this research.

The SEM images of BST powders obtained by the heat treatment of the precursor powders with NH_4NO_3 as combustion promoter and without NH_4NO_3 are shown in Fig. 4. Particles calcined with combustion promoter addition are of a narrow size distribution of 60–90 nm with clear surface as well as dispersive and homogeneous, as shown in Fig. 4 (a). Comparatively, particles calcined without

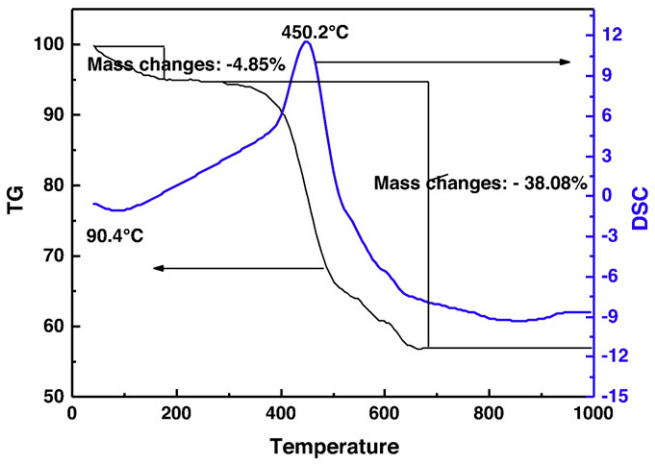

Fig. 2. TG-DTA curves of the precursor powders obtained in flowing air with a heating rate of 10 °C/min.