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Structural characterization of $Ba_{1-x}Sr_xTiO_3$ (BST) nanopowders prepared by stearic acid gel method

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ABSTRACT

Stoichiometric tetragonal Ba1-xSrxTiO3 (x = 0.23) nanopowders were prepared by stearic acid gel (SAG) method using barium stearate, strontium stearate, tetrabutyl titanate as Ba, Sr, Ti sources and stearic acid as complexing reagent. Thermal analysis including differential thermogravimetric (DTG) and TG, Fourier transform infrared spectrometry (FTIR), X-ray diffraction (XRD) and transmission electron microscopy (TEM) were used to characterize the crystallization process, particle size and morphology of the calcined powders. The results indicated that single- phase tetragonal and well crystallized Ba1-xSrxTiO3 (x = 0.23) nanopowders with particle size around 45 nm were formed after calcining the dried gel at 700 °C for 2 h.
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Keywords: Ba1-xSrxTiO3; Nanopowders; Wet route synthesis; Stearic acid gel method

INTRODUCTION

Barium strontium titanate (i.e., Ba1-xSrxTiO3 or BST) is one of the most interesting materials due to its pyroelectric, ferroelectric and piezoelectric characteristics, has been widely used in the preparation of high dielectric capacitors, PTC (Positive Temperature Coefficient) resistors, transducers and ferroelectric memories [1–6].

BST powders are usually prepared by solid-state reaction [7- 8] with calcination temperatures in the range of 1300–1450 °C which produce large BST particles with uncontrolled morphologies due to their inherent problems such as high reaction temperature, heterogeneous solid phase reaction, etc.

By contrast with the traditional methods, the wet-chemistry synthesis techniques, including the hydrothermal method [9], precipitation method [10], metalorganic solution deposition (MOSD) technique [11] and the sol–gel method [12-13] have been reported. The sol gel route, is proved to be a very commonly applied chemical method for fabricating uniform large area thin films and synthesizing powders of micrometer, sub-micrometer or nanometer size with high purity and homogeneity. However, the sol gel process necessitates expensive and unstable metal alkoxides and needs long refluxing time.

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In this paper, we present a typical wet-chemistry synthesis method using stearic acid gel (SAG) to prepare pure and uniform fine BST nanopowders. In this method, the carboxylic acid group with the long carbon chain in stearic acid, endow strong ability to disperse metal ions precursors and the process can be easily controlled and leads to the uniform fine nano-powders.

EXPERIMENTAL

$Ba_{1-x}Sr_xTiO_3$ (x = 0.23) nanopowders were synthesized along a synthetic procedure as summarized in Fig. 1. The raw materials used in the experiment, barium stearate, strontium stearate, tetrabutyl titanate and stearic acid, were of analytical grade reagents. Exactly 0.2 mol of stearic acid was first melted in a beaker at 73 °C, and then stoichiometric amount of barium stearate and strontium stearate (0.035 and 0.015 mol respectively) was added to the melted stearic acid and dissolved to form a yellow transparent solution. Then, 0.05 mol tetrabutyl titanate was added to the solution, stirring to form a homogeneous sol, naturally cooling down to room temperature, and drying in an oven for 12 hrs to obtain the gel. Finally, the gel was calcined at different temperatures in air to obtain nano-crystallites of BST.

The process of formation and structural characterization of BST phases have been investigated by TG /DTG, FTIR, XRD, and TEM. Thermogravimetric and differential TG analysis experiments were performed on a TG/DTA METTLER TA 4000 instrument in air to investigate possible phase transformations from 25 to 900° C with a heating rate of 5 °C/min. The FTIR spectrum was recorded with an MB100 (BOMEM) spectrometer by using KBr pellet. The XRD patterns were recorded on a SEISERT Argon PTS 3003 diffractometer using Cu K□ radiation (λ=1.5418A°) in the range from 10° to 90° (2θ) to examine the crystallization and structural development of BST powders. The TEM pictures were recorded on a Philips EM 208 microscope operated at 100 kV. The samples were prepared by dispersing the fine powder in amyl acetate. Imaging was enabled by disposing few drops of suspension on a carbon coated 400 mesh Cu grid.

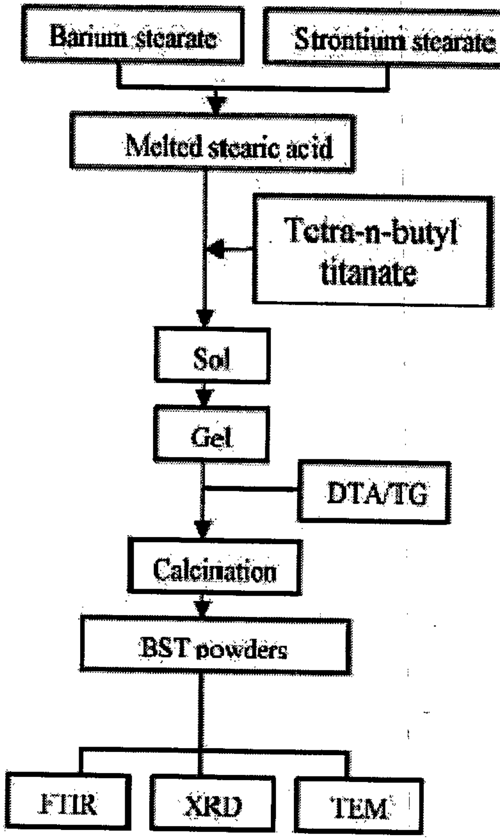

Fig. 1. Flowchart for the preparation of BST nanopowders.

RESULTS AND DISCUSSION

Thermal analysis

In order to investigate the synthesis process for BST nanopowders, TG/DTG analysis was performed on dried gel samples and the results are shown in Fig. 2. The DTG curve, at the first step, reveals a weight loss between 124-245 °C, due to the evaporation of volatile components and in the second step, a drastic weight loss (46.76 %) at the temperatures between 245-371°C and 371-460 °C assigned to the combustion of the organic derivatives in the gel and formation of metal carbonate, BaCO3 and Ti(IV) complex (the boiling point of stearic acid is 383°C.) The last and fairly weak broad pick, corresponding to the 13.56 % weight loss starting from 460 °C to 520 °C was assigned to the formation of BaCO3 and Ti(IV) complex from disordered state to ordered stat and small amount of BaTiO3 was produced. Finally, the weak and broad range of weight loss occurred at the temperature between 520 °C - 640 °C, indicating that nearly all of the BaCO3 reaction with Ti complex produce BaTiO3, releasing of CO2. No apparent peak and significant weight loss was observed at the temperature over 640 °C, indicating the minimum crystallization temperature to prepare BST nanopowders. The process and generated species in each step were confirmed by corresponding XRD patterns in Fig. 3.

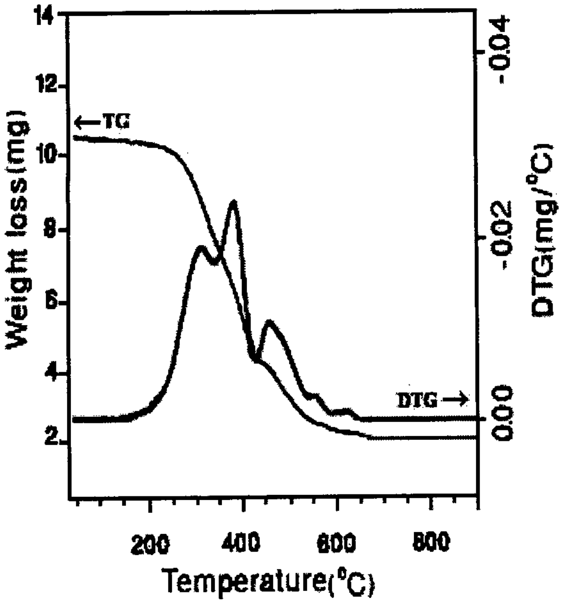

Fig.2. TG/DTG curves of uncalcined BST dried gel.

3.2. X-ray diffraction patterns and IR spectra

The above cited phase formation, starting from the BST precursors, was confirmed by means of XRD. The Fig.3. shows the XRD patterns of BST precursors after heat-treatment from 450 oC to 700 °C in air for 2 h. The diffraction peaks (*marked peaks) at 24.08, 34.28 and 42.3(2θ) corresponding to the impurity phase of barium carbonate (JCPDS, File No. 01-0506) appeared for the powders calcined at 450°C (Fig.3a). By increasing temperature, the perovskite-like phase crystallization was initially started after calcining the dried gel at 550 °C with an impurity phase of barium carbonate (Fig.3b). The intensity of the diffraction peaks of $BaCO_3$ decrease with increasing calcinations temperature and finally, the high purity tetragonal perovskite of $Ba_{1-x}Sr_xTiO_3$ (x = 0.23) nanopowders were obtained at 700 °C (Fig.3c). All the peaks corresponding to tetragonal phase and their intensities were well matched with database in JCPDS, File No. 44-0093. The crystallite size of the particles calcined at 700 °C is calculated by the Scherrer's equation: $D=k\lambda/\beta \cos\theta$, where D is the crystallite size, k is a constant (0.9, spheres), λ is wavelength of the X-ray radiation, β is the line width obtained after correction for the instrumental broadening and θ is the angle of diffraction. The crystallite size obtained from XRD data (700°C) is 45nm.

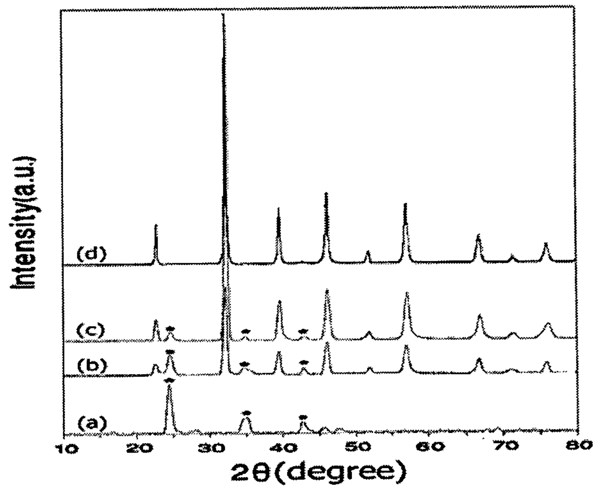

Fig. 3. X-ray diffraction patterns of BST at (a) 450, (b) 550, (c) 600 and (d) 700 °C.

The BST nanopowders formation was further supported by FTIR spectrum as shown in Fig. 4. The FTIR spectrum of the BST sample prepared by SAG method, calcined at 700 °C showed broad main bands at around 3400-3200, 1620 and 570 cm^{-1} , which can be assigned to ν_{O-H} , δ_{HO-H}, and ν_{Ti-O} vibrations respectively. Two other bands observed at around 1420 and 1050 cm^{-1} can be ascribed to the asymmetric and symmetric stretching vibrations of carbonate, $\nu_3(CO_3)$ and $\nu_1(CO_3)$ ions formed

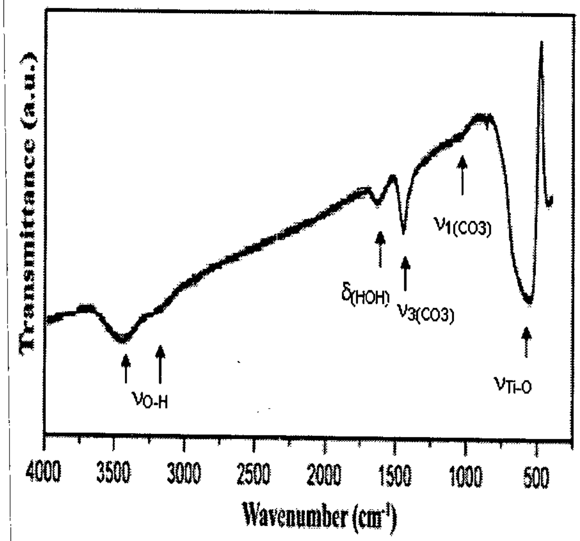

Fig.4. FT-IR spectra of the powders calcined at 700 °C.

during decomposition of stearate groups and organic derivatives. Presence of minimal $BaCO_3$ in the sample may be caused by excessive barium resource introduced in raw materials and the FTIR spectrum was found to be by far the most sensitive technique to identify minimal $BaCO_3$ in which the quantity as small as 0.1 wt% can be detected [14].

Morphology of samples

The morphology and crystalline structure of the calcined BST nanopowders were further investigated by TEM. TEM images show the $Ba_{1-x}Sr_xTiO_3$ sample calcined at 700 °C (Fig.5). The particle size of BST calcined at 700 °C was estimated to be in the range of 40- 80 nm. This grain size in this temperature seems to be in consistent with the XRD results calculated by Scherrer's formula (45 nm).

CONCLUSIONS

We have produced high purity stochiometric $Ba_{1-x}Sr_xTiO_3$ (x = 0.23) nanopowders using wet-chemistry synthesis route through stearic acid gel (SAG) techniques. The synthetic process was easily controlled and convenient in comparison with other methods. Tetragonal phase BST nanopowders with perovskite structure were initially formed after calcining the dried gel at 550 °C and the high purity tetragonal perovskite of $Ba_{1-x}Sr_xTiO_3$ (x = 0.23) was obtained after calcining at 700 °C for 2h. The particle size of the BST nanopowders calculated by Scherrer's formula was estimated in the range of 40- 80 nm.

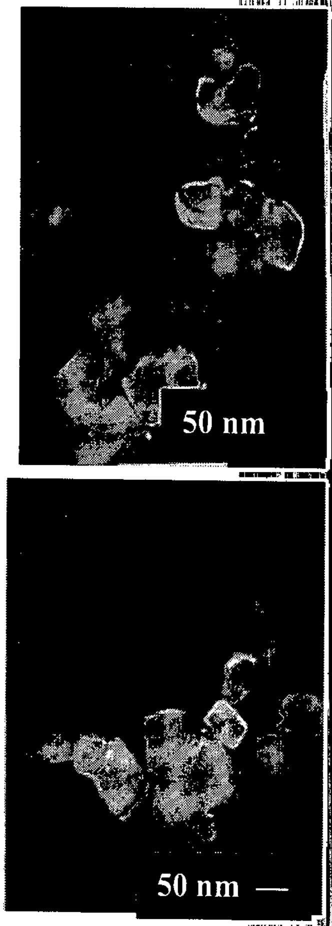

Fig.5. TEM images of BST nanopowders calcined at 700 °C for 2 h.

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