SYNTHESIS AND DIELECTRIC PROPERTIES OF NANOCRYSTALLINE BASRTIO₃

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Ba_{0.7}Sr_{0.3}TiO₃ was prepared via simple sol-gel method by using titanium tetrabutoxide, barium and strontium carbonates, citric acid and ethylene glycol as starting materials. Simultaneous Thermal Analysis (STA) was used to examine thermal behavior of xerogel. The crystallite size of BST was about 21nm calculated by X-Ray diffraction (XRD) and confirmed by transition electron microscopy (TEM). Using these nanocrystalline powders, BST pellets were prepared and sintered in various temperatures. The grain size effect on electrical properties was studied and found that as the grain size decreased, the dielectric constant decreased too.

Keywords: (Ba,Sr)TiO₃; Sol-Gel; Nanocrystalline; Dielectric properties.

1. Introduction

Barium-strontium titanate is a kind of favorable electronic material because of its high dielectric constant and variable Curie temperature with composition.¹ It has been found that BST has applications in large areas such as piezoelectric sensors, dynamic random access memories (DRAM), microwave phase shifters and uncooled infrared detectors for its high dielectric, ferroelectric, and pyroelectric properties.²⁻⁴ In order to gain the desired electrical characteristics, high chemical purity and uniform microstructure are the most important features for BST ceramics. Furthermore, the outstanding dielectric property observed on fine-grained BST ceramics has motivated the interest for the synthesis of the nanocrystalline BST.

To achieve fine microstructure and high performance, it is necessary to start with preparing fine, stoichiometric and narrow size distribution powder. For this purpose, several wet chemical non-conventional methods such as sol–gel, self-propagating high-temperature synthesis and hydrothermal techniques were proposed as alternative method for dry mixed-oxides synthesis to improve microstructure homogeneity & chemical reaction at lower temperature.⁵⁻¹⁰

This paper presents a simple process for synthesis of nanocrystalline BST powders and sintering fine-grain BST.

2. Experimental

2.1. Materials & methods

Flowchart of the process has been shown in Fig. 1. The precursor solution was prepared by using barium carbonate (99.0%), strontium carbonate (98.0%), tetrabutyl titanate (98%), citric acid (99.5%), and ethylene glycol (EG) as starting materials.

Fig. 1. Flow chart for synthesis of BST nanoparticles.

First, 0.1 mol of Ti (C₄H₉O)₄ was dissolved into 2 mol of ethylene glycol. The mixture was stirred for about 3 min to be dissolved. Subsequently, 0.5 mol Citric acid powders and 0.1 mol water were added to this solution and was stirred for 20 min on a magnetic stirrer. Then, 0.07 mol BaCO₃ and 0.03 mol SrCO₃ powders were added to this solution. Then the solution was stirred in water bath at 75°C. Finally, solution was heated

to 130°C for 11h. The xerogel was heated in 300°C for 2 h and subsequently it was calcined at different temperatures for 100 min.

Ceramic samples were obtained by pressing the powders into pellets of 10mm diameter under 250MPa pressure, and then sintered in air at 1150-1400 °C for 4 h, and 1200 °C for 10 h.

2.2. Characterization

Xerogel were analyzed by STA (PL1640) under static air with a heating rate of 10°C/min from room temperature to 1000°C. X-ray diffraction (XRD) with Cu K α radiation (Philips PW3710) was carried out to examine the phase composition of obtained BST powders. The microstructure of the BST powders was investigated by transmission electron microscopy (Philips EM208). The morphology of the sintered compacts was studied using a scanning electron microscopy (Vega Tscan). Dielectric properties were measured by impedance–capacitance– resistance (LCR) meter (41R) at 120 Hz, 1 KHz and 10 KHz using Ag as the electrode on both faces of the samples.

3. Results and discussion

In order to seek the synthesis temperature of BST powders, STA measurements were made on the xerogel. STA results in Fig. 2 indicates there were three decreases in the sample weight over the temperature ranges of 31–108, 108–630 and 630–830 °C. 3.9% weight loss was in the first step corresponding to the endothermic peak at 98°C can be attributed to the evaporation of absorbed water from atmosphere. The next step with a weight loss of 83.5% was recorded for the decomposition of the citrate precursor.

At the beginning part of this weight decrease an endothermic peak at 155°C was attributed to the decomposition or removal of the organic parts which combined weakly with others in the precursor.

On the other hand, the corresponding three exothermic peaks around 275, 480 and 623°C can also be attributed to the drastic combustion of the organic species involved in the precursor. 1.5% loss of mass during the last step, accompanied by an endothermic peak at 713 °C which corresponded to the decomposition of residual carbonate.

Figure 3 shows the XRD patterns of BST powders prepared at different temperatures. It can be seen in 700°C, there was a weak peak appearing at 24.2 corresponding to the residual carbonates phase, such as BaCO₃, SrCO₃ and (Ba,Sr)CO₃.^{11,12} At higher temperatures, these peaks disappeared and a pure BST phase was obtained at 750°C & 800°C because of complete decomposition of residual carbonates. Absence of any weight changes and peak after 713°C in STA result in Fig. 2 is in good correspondence with these results.

Figure 4 shows the TEM image of the particles obtained at 750°C. Most of the powders were rectangular. Average size of the ultimate particle was found to be 19 nm approximately. This value was consistent with the result calculated by XRD (21 nm) using Scherrer's formula.

Fig. 2. STA curves of the xerogel in static air from room temperature to 1000 °C.

Fig. 3. XRD patterns of the BST powders synthesized at different temperatures.

The densities of sintered samples have been shown in Fig. 5. Highly dense BST body (the relative density is about 99%) was obtained when sample was kept 4hr at 1350°C. The average grain size was about 2.9μm and the grains were not homogenized.

Fig. 4. TEM image of nanocrystalline BST powders obtained at 750 °C.

Fig. 5. Density and grain size of sintered samples in different temperatures.

Figure 6 shows the fracture surface of sintered sample at 1350°C for 4 hr and also sintered sample at 1200°C for 10 hr (the relative density was about 99%). For sintered sample at 1200°C for 10hr the average grain size was about 650nm.

Fig. 6. Morphology of sintered ceramics on the fracture surface (a) sintered at 1350 °C for 4h (b) sintered at 1200°C for 10h.

The temperature dependence of the dielectric constant (k) of BST ceramic sintered in 1350°C for 4hr is shown in Fig. 7(a). For comparison, Fig. 7(b) shows the dielectric constant of sample which sintered at 1200 °C for 10h.

Fig. 7. Dielectric constant vs. temperature (a) BST ceramic sintered in 1350°C for 4hr (b) BST ceramic sintered in 1200°C for 10hr.

Table 1 shows the dielectric constant of different grains size under different frequencies at room temperature.

Table 1. The dielectric constant of different grain size under different frequencies at room temperature.

Frequencies	Dielectric Constant	
	2.9 μm , 27°C	650 nm, 27°C
120Hz	9447	6680
1kHz	9247	6572
10kHz	8813	6357

It can be seen that the dielectric constants of the two samples decreased when the frequency increased. But the decrease of the dielectric constant for the fine-grained sample was less than that of the coarse-grained one. This implies the better stability of dielectric constant versus frequency of fine-grained sample. Furthermore, the maximum value of k was smaller than that of the coarse-grained ceramics. This could be attributed to the total effects of the internal stress, grain boundary and domain wall contributions to the dielectric constant, which was similar to the result of A.S. Shaikh et al. for BaTiO_3 .^{13,14}

4. Conclusion

Fine BST nanoparticles, with an average particle size of 20 nm, were successfully synthesized by a simple sol-gel process. Pure phase BST could be obtained at 750°C. It has been shown that highly-dense BST will be obtained with heating at 1350°C for 4h. Fine-grain BST ceramic with high density will be obtained by heating at 1200°C for 10h. The average grain size of the ceramic was about 650 nm. Compared to the relatively coarse-grained BST, the fine-grained sample exhibits the better stability of dielectric constant versus frequency. Dielectric data show a broad phase transition and decreased value of k due to the fine-scaled grains. This low-temperature and simple synthetic route requiring only simple raw materials, and also the low temperature sintering will offer a new strategy to obtain fine-grain BST.

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