Ceramics International xxx (xxxx) xxx–xxx

Contents lists available at ScienceDirect

Ceramics International

journal homepage: www.elsevier.com/locate/ceramint

Enhanced energy storage performance of $Ba_{0.4}Sr_{0.6}TiO_3$ ceramics: Influence of sintering atmosphere

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ARTICLE INFO

Keywords:
Powders: chemical preparation
Grain size
Dielectric properties
Perovskites

ABSTRACT

$Ba_{0.4}Sr_{0.6}TiO_3$ (BST) powders were prepared by hydrothermal method, the ceramics were sintered in N_2, air and O_2 atmosphere respectively. The effect of sintering atmosphere on the microstructure, dielectric properties, and energy storage performance of BST ceramics were investigated. The grain size of the BST ceramics sintered in O_2 atmosphere was reduced to 0.44 μm, indicating the grain growth was significantly inhibited with increasing oxygen partial pressure due to the lack of oxygen vacancy. Dielectric relaxation behavior was observed in the BST ceramics, and the degree of which was increased with increasing oxygen partial pressure. BST ceramics sintered in O_2 atmosphere showed the largest critical breakdown strength of 16.72 kV/mm, at which the highest energy storage density of 1.081 J/cm^3 and a moderate energy storage efficiency of (73.78%) were obtained. The dependence of energy-storage properties on applied field was also investigated, it was found that the energy storage density increased with increasing applied filed while the energy storage efficiency decreased with increasing applied filed.

1. Introduction

Advanced energy storage electronics are becoming increasingly important to applications with the demand of the modern pulsed power technology in the field of power distribution and transportation [1,2]. Especially, ceramic capacitors have been focused on energy storage applications because of their high power density, high reliability, numerous times of circling use, and extremely short charging/discharging period [3,4]. Among them, $(Ba_xSr_{1-x})TiO_3$ attracts many attentions due to its high power density and good electrical reliability. The Curie temperature (T_c), phase structure, and electrical properties of $(Ba_xSr_{1-x})TiO_3$ can be controlled by the mole fraction of Sr^{2+} to satisfied specific applications. $(Ba_{0.4}Sr_{0.6})TiO_3$ (BST) ceramics possess excellent dielectric properties of high dielectric constant, low dielectric loss and high stable dielectric properties at room temperature, furthermore, the high polarization and low hysteresis loss of BST are promising for electric energy storage applications [5,6]. However, the energy storage performance of BST ceramic is strongly limited by its low dielectric breakdown strength (BDS), since the high energy density in the dielectrics relies more on the high breakdown strength, according to the energy density equation for nonlinear dielectrics [7,8].

In recent years, a great number of works have been done to increase the BDS of the BST ceramics: glass additives in BST ceramics are believed to decrease the sintering temperature and refining the microstructure [9], Wu et al. [5] doped $BaO–TiO_2–SiO_2$ glass-ceramics into BST ceramics, successfully improved the BDS from 9.19 kV/mm to 16.51 kV/mm, however the saturated polarization (P_s) decreased significantly, so the energy storage density only increased from 0.37 J/cm^3 to 0.59 J/cm^3 [5]. Wang et al. [10] obtained the $BaO-B_2O_3-SiO_2-Na_2CO_3-K_2CO_3$ glass-modified $(Ba_{0.4}Sr_{0.6})TiO_3$ ceramics with the energy storage density of 0.7 J/cm^3 at 15 kV/mm [10]. From these works, it seems insufficiently for glass additives to enhance the energy storage performance of the BST ceramics. On the contrary, efforts focused on the sintering process of BST ceramics show relatively good results: Song et al. [4] prepared $Ba_{0.4}Sr_{0.6}TiO_3$ by post annealed microwave sintering and obtained the energy storage density of 1.15 J/cm^3 at 18 kV/mm [2]. Huang et al. obtained $Ba_{0.4}Sr_{0.6}TiO_3$-MgO ceramics using spark plasma sintering with the energy storage density of 1.5 J/cm^3 at 30 kV/mm [6]. These works indicate that the sintering process has a great influence on the misconstrue and electrical properties of the BST ceramics.

The existing literature reported that sintering atmosphere plays a very important role in determining microstructures and electrical properties of oxide ceramics since the effect of oxygen vacancies [11,12]. It has been found that the structural transition of grain boundary and related grain growth behavior of $BaTiO_3$ ceramics were closely related to oxygen partial pressure during sintering, and the grain size was reduced in the oxygen sintering atmosphere [11]. Wang

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http://dx.doi.org/10.1016/j.ceramint.2017.05.229

et al. [10] reported that the grain size of $Sr(Fe_{0.5}Nb_{0.5})O_3$ ceramics decreases with increasing oxygen partial pressure [12]. These works give us the inspiration of using different sintering atmosphere to modified the microstructure and electrical properties of BST ceramics. However, few work about the BST ceramics sintered in various atmosphere are reported.

Therefore, in this study, BST ceramics sintered in N_2, air and O_2 atmospheres were prepared respectively, with hydrothermal synthesized BST powders as raw materials. Microstructure, dielectric properties and energy storage performance of BST ceramics were investigated.

2. Experimental

The BST powders were prepared via hydrothermal method with $Sr(NO_3)_2$, $TiCl_4$ and $BaCl_2$ as raw materials, and KOH as mineralizing agent. Starting materials $Sr(NO_3)_2$ and $BaCl_2$ were added to distilled water containing of KOH and stirred for 1 h until it became a miscible clear solution. Then $TiCl_4$ was dropwise added and stirred for 1 h. The precursor was poured into the Teflon lined pressure vessel and then placed in a pre-heated oven at 200 °C for 8 h. The obtained powders were washed 10 times using distilled water. Then dried and gain $Ba_{0.4}Sr_{0.6}TiO_3$ powders. The powders were pressed into disk shaped pellets and sintered in nitrogen, air and oxygen atmosphere respectively.

The crystallization behavior of the samples was investigated by powder X-ray diffractometry (D-MAX 2200pc, Rigaku Co, Tokyo, Japan). The microstructure observation of the samples was carried out using field-emission scanning electron microscope (SEM; Hitachi S4800, Japan). The dielectric properties of the ceramics were measured using a precision LCR Meter (E4980A, Agilent Tech, CA, US) over a frequency range from 100 Hz to 100 kHz. The polarization-electric field (*P-E*) loops were measured using a ferroelectric test system (Premier II, Radiant, USA) at room temperature.

3. Results and discussion

The BST powders were successfully synthesized via hydrothermal method with good crystalline and no other phases, as can be seen in Fig. 1(a), it could also be seen that the powders were typical cubic perovskite structure. Fig. 1(b) shows the SEM image of the hydrothermal synthesized BST powders. The particles are spherical in nature and less agglomerated and the particle distribution is uniform. To investigate the particle distribution, the particle size was statistically calculated on Fig. 1(b) by Image Pro Plus software and the results were plotted in Fig. 1(c). The average particle size is 51.71 nm, and are mainly located in the range from 40 to 60 nm (77%), which indicates the uniform distribution of the BST particles.

Fig. 2(b) shows the XRD patterns of the BST ceramics which clearly indicate the formation of pseudocubic phase perovskite structure without any secondary phase in spite of the sintering atmosphere. The lattice parameters of samples are calculated by cell refinement. The results show that the lattice parameters (a = b = c) of BST sintered in N_2, air and O_2 is 3.91707 Å, 3.91791 Å and 3.91825 Å, and the unit cell volume is 60.10 $Å^3$, 60.14 $Å^3$ and 60.16 $Å^3$ respectively. It can be found that the unit cell volume increases with increasing oxygen partial pressure, suggesting the oxygen vacancies might reduce the lattice parameters. SEM images measured on the natural surface of the BST ceramics are shown in Fig. 2(b, c, d). It can be seen that all samples are well densified with no pore, and the grain size of the BST ceramics sintered in O_2 decreases significantly, indicating the increase of oxygen partial pressure can remarkably inhibit the growth of the grains in BST ceramics.

In order to investigate the grain size distribution of the BST ceramics sintered in different atmosphere, the grain size distributions of BST ceramics were carried out using Image Pro Plus software, the statistics results were plotted in Fig. 3. The average grain sizes were estimated in the light of the grain size distribution. The average grain size of BST ceramics sintered in N_2 and air were 1.11 μm and 1.09 μm, and for sample sintered in O_2, the average grain size decreased to 0.44 μm. Furthermore, the grain sizes of samples sintered in N_2 and air are mainly distributed in the range from 0.7 μm to 1.5 μm, for samples sintered in O_2, the distribution range were obviously narrowed to the range of 0.35–0.55 μm, which meant the much more homogeneous microstructure of the BST ceramics. As was generally recognized [13], when the oxygen partial pressure was very low in the sintering atmosphere, oxygen atoms separated from the ceramics lattice, and thus the oxygen vacancies formed at the grain boundaries. The presence of oxygen vacancies in oxide materials was beneficial to ion transport during sintering [14]. This should be responsible for the promoted grain growth in BST ceramics sintered in N_2. As the oxygen partial pressure increased, oxygen vacancies decreased gradually, which led to the grain growing slowly, so the average grain size decreased.

The temperature dependent of dielectric properties for BST ceramics sintered in different atmosphere are given in Fig. 4. The dielectric loss of the samples decreases with temperature, and is all under 0.02 at room temperature. The curie temperature of the BST ceramics sintered in N_2, air and O_2 is 202.72 K, 203.69 K and 202.44 K respectively, corresponding to the phase transition from tetragonal to cubic phase. There is also a lower peak located in the left of the curie temperature, which represent the phase transition temperature of orthorhombic to tetragonal phase. It is worthy noted that for BST ceramics sintered in O_2, as the grain size reduced from 1.09 μm to 0.44 μm, dielectric constant around the Curie temperature decreases significantly, with a clear tendency toward a diffuse phase transition, which was thought to be inherently associated with the internal stress between grains [15].

It can also be seen that all curves of the three samples show the ferroelectric relaxor characteristic of a diffuse phase transition, a decrease in the value of the permittivity as a function of frequency

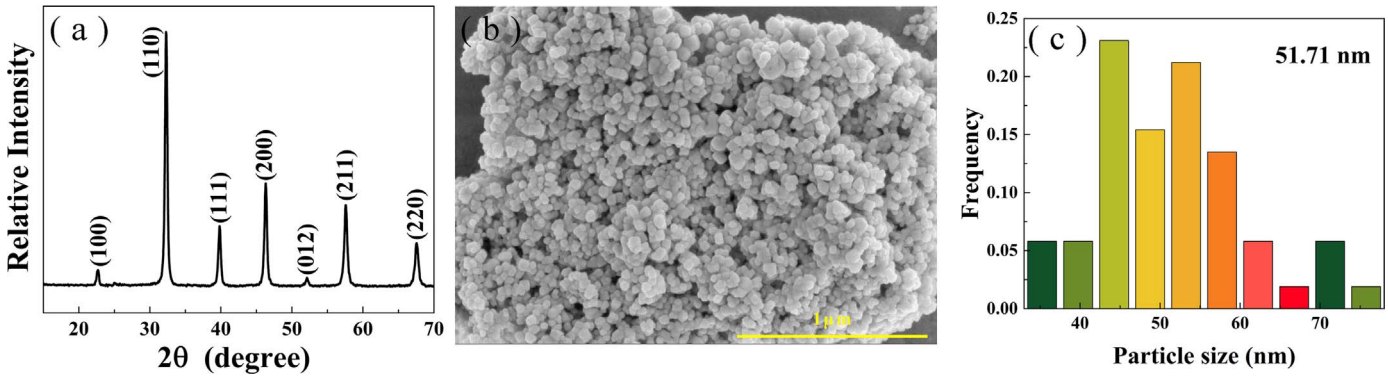

Fig. 1. (a)XRD pattern, (b) SEM image and (c) particle size distribution of the hydrothermal synthesized BST powders.