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Combustion synthesis of nanostructured $Ba_{0.8}(Ca,Sr)_{0.2}TiO_3$ ceramics and their dielectric properties

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Abstract

$Ba_{0.8}(Ca,Sr)_{0.2}TiO_3$ nanostructured ceramics were synthesized by a facile and glycine-assisted auto-combustion method using stable solid TiO_2, which is better than other several chemical routes reported earlier involving expensive alkoxides, oxynitrates, or chlorides of titanium as the titanium sources. TGA/DSC analysis of precursor powder gives pre-information about formation of final product around 950 °C. XRD analysis confirms the formation of single-phase of the BCT and BST ceramics on sintering at 950 °C for 15 h. TEM image of the ceramics show nanocrystalline particles in the range 40–90 nm. Surface morphology indicates that the average grain size is in range of 55–140 nm and 45–120 nm for BCT and BST, respectively. Energy dispersive X-ray spectroscopy and X-ray photoelectron spectroscopy confirmed the purity and stoichiometry. The value of the dielectric constant of BST ($\varepsilon_r \sim 368$) ceramic is higher than BCT ($\varepsilon_r \sim 255$) at 100 Hz at 308 K. The dielectric constant BST is higher than BCT at all measured temperatures and frequency ranges due to higher crystallinity and high grain-boundary resistance, as confirmed by impedance analysis.

Keywords: C. Dielectric properties; D. Perovskite; Combustion synthesis; Nanostructured

1. Introduction

In recent years, materials with submicron and nanosized structures have attracted considerable interest owing to their unusual dielectric [1,2], mechanical [3], electrical [4], and magnetic properties [5]. In the development of device miniaturization, high density data storage systems, microelectronics, and other related fields have led to the constant miniaturization and further reduction of the crystallite size below the micrometer scale. One of the most important is powder synthesis with a nano-size range (≤ 100 nm), a controlled stoichiometry and well-defined properties [6,7]. Ferroelectric ceramic, $BaTiO_3$ are used in capacitor devices [8], piezoelectric devices [9], transducers [10], and thermistors [11]. Ceramic capacitors based on ferroelectric materials have very high capacity and a small size, which enable the miniaturization of electronic devices. Over the past decade, extensive studies on the synthesis of nano-sized $BaTiO_3$ powders with a narrow particle size distribution, controlled morphology and high purity have been conducted [12]. Several methods, such as conventional solid state routes [13,14], co-precipitation [15], hydrothermal technique [16] and sol–gel [17–19] have been used for the synthesis of ferroelectric $BaTiO_3$ ceramics. Solution combustion synthesis (SCS) is an effective synthesis technique for nanostructured materials, and has been used in the production of various ceramic powders [20]. This technique was used to prepare ceramics via the combination of metal nitrates in an aqueous solution with fuels, such as glycine, citric acid and urea [21]. The solution combustion synthesis has been chosen

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Table 1
Precursors used in the sol–gel synthesis method, metal dopant, of the $BaTiO_3$ ceramics.

Barium	Titanium	Metal dopant	Ref.
$(CH_3CO_2)_2$ Ba	Titanium (isopropoxide)	Cerium	[23]
$Ba(OH)_2.8H_2O$	Titanium (isopropoxide)	–	[24]
$(CH_3CO_2)_2$ Ba	Titanium butoxide	neodymium	[25]
$(CH_3CO_2)_2$ Ba	Titanium butoxide	–	[26]
Barium acetylacetonate	Titanium (isopropoxide	–	[27]
Barium acetate	Titanium tetrabutoxide	–	[28]
$Ba(OH)_2$	Tetrabutyl titanate	–	[29]
$Ba(OH)_2 \cdot H_2O$	Titanium butoxide	–	[30]
$Ba(CH_3COO)_2$	Tetrabutyl titanate	–	[31]

for the fabrication of $BaTiO_3$ because of its many advantages, such as fine particle size, simple compositional control and low processing temperatures [22]. As discussed above, the literature on the solution based synthesis up to date used very expensive alkoxide, oxynitrate, or chlorides of titanium as the titanium sources, which are very difficult to handle. Therefore, is important to develop a simple, ecofriendly and inexpensive chemical route for the fabrication of nano-structured $BaTiO_3$ ceramic.

This research article reports the simple, inexpensive and effective synthesis of nano-structured Ca ($Ba_{0.8}Ca_{0.2}TiO_3$, BCT) and Sr ($Ba_{0.8}Sr_{0.2}TiO_3$, BST) doped $BaTiO_3$. The doped $BaTiO_3$ ceramics fabricated via a glycine-assisted auto combustion process, applying inexpensive and stable solid TiO_2 powder as the titanium source. The proposed fabrication process can be controlled easily and is convenient compared to other chemical routes. The BCT and BST ceramics obtained by this processes were characterized by TGA/DSC, XRD, TEM, SEM, EDX, and XPS techniques, along with measurements of their dielectric and electrical properties.

2. Experimental

2.1. Material synthesis

Nano-structured $Ba_{0.8}Ca_{0.2}TiO_3$ and $Ba_{0.8}Sr_{0.2}TiO_3$ ceramics were prepared by glycine-assisted combustion synthesis using analytical grade chemicals, $Ba(NO_3)_2$ (98%, Daejung), $Ca(NO_3)_2.4H_2O$ (97%, Daejung), $Sr(NO_3)_2$ (98%, Daejung), glycine (99%, Daejung) and economical TiO_2 (99.9%, Sigma Aldrich), in solid state form without any specification of the phase and particle size as starting materials. Table 1 lists the chemical precursors used in the sol–gel synthesis method, metal dopant and the $BaTiO_3$ ceramics. All the earlier chemical syntheses reported the used of very expensive titanium sources for the fabrication of $BaTiO_3$ [23–31]. The molar concentrations of metal nitrates, stoichiometric amount of glycine, solid TiO_2 and sintering parameters used for the synthesis of BCT and BST are listed in Table 2. In this method, metal nitrates were dissolved in doubly distilled water to obtain the standard aqueous solutions of Ba^{2+}, Ca^{2+} and Sr^{2+}. Stoichiometric amounts of the standard aqueous solutions of Ba^{2+} and Ca^{2+} used in the synthesis of BCT and Ba^{2+} and Sr^{2+} for BST

Table 2
Experimental conditions for the synthesis of BCT and BST ceramics.

Specimen	Metal	Concentrations	Calcination temp. (°C)/duration (h)	Sintering temp. (°C)/duration (h)
$Ba_{0.8}Ca_{0.2}TiO_3$	Ba	0.0138708 (g/mL)		
	Ca	0.0040897 (g/mL)	800/8	950/15
	TiO_2 (solid	3.995 (g)		
	Glycine	7.507 (g)		
$Ba_{0.8}Sr_{0.2}TiO_3$	Ba	0.0138708 (g/mL)		
	Sr	0.0088504 (g/mL)	800/8	950/15
	TiO_2 (Solid)	3.995 (g)		
	Glycine	7.507 (g)		

were mixed in separate beakers along with stoichiometric amounts of solid TiO_2. Subsequently, glycine (equivalent to metal ions) was added to the solutions. The resulting dispersion was heated on a hot plate with continuous stirring at 70–90 °C to evaporate the excess water. During the evaporation, the heterogeneously mixed solution initially turned viscous and eventually into a gel. The formed gel slowly foamed, swelled and finally burnt on its own. The combustion process was carried out in air and burnt under self-propagating combustion, which exhausted large amounts of gases and produced a fluffy mass of BCT and BST ceramic powders. The foamy products of BCT and BST were collected and calcined in air at 800 °C for 8 h in an electrical furnace. The calcined powders of BCT and BST were mixed with 2 wt% polyvinyl alcohol (PVA) and pressed into cylindrical pellets using a hydraulic press. The PVA binder was burnt out at 350 °C for 2 h. Finally, the BCT and BST pellets were sintered at 950 °C for 15 h in air. A schematic flow chart of the synthesis processes is shown in Fig. 1.

2.2. Material characterization

Simultaneous thermogravimetric analysis/differential scanning calorimetry (TGA/DSC) of the precursor powders were performed on a SDT Q600 (V20.9 Build 20) instrument. The sample was put into an alumina crucible and was heated in N_2 at 10 °C min^{-1} from room temperature to a final temperature of 1000 °C. X-ray diffraction (XRD, Ultima IV, Rigaku, Japan) of the sintered BCT and BST pellets was performed using Cu Kα radiation ($\lambda = 1.5406$ Å) at 40 kV and 30 mA over a 2θ range, 20–80°, in continuous scan mode at 2 ° min^{-1}. The microstructural features of the ceramics were examined by field emission scanning electron microscopy (FESEM, JSM6500F, Jeol, Japan), and the particle size was evaluated using a high resolution transmission electron microscopy (TEM, JEM 2100F). An energy dispersive X-ray analyzer (EDX, model Kevex, Sigma KS3) attached to the SEM was used for elemental analysis. The specimen for TEM