Direct synthesis of Y doped BaTiO$_3$ powder by sol-precipitation method

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Ultra fine and homogeneous BaTiO$_3$ doped with 0.5 at% yttrium powder was prepared by sol-precipitation method using barium acetate, titanium (IV) diisopropoxide bis-acetylacetonate and yttrium (III) butoxide as starting precursors. The effect of pH value on the precipitate formation from the sol is pointed out in this paper. The grain size of the precipitate was about 100-200 nm. The structural evolution of the precursor precipitate as function of temperature was investigated. Ba$_{0.995}$Y$_{0.005}$TiO$_3$ single phase was obtained at 1300 °C. The ceramics manufactured from the as-prepared powder presented good dielectric characteristics (dielectric constant = 2152 and dielectric loss (tanδ) = 4.54% at the Curie temperature of 125 °C). These ceramics are expected to be useful in dielectric applications.

1. Introduction

Barium titanate is one of the widely used material for electric ceramics due to its excellent dielectric [1], ferroelectric [2, 3], and piezoelectric properties [4].

Yttrium doped BaTiO$_3$ ceramics prepared from a mixture of BaCO$_3$, TiO$_2$ and Y$_2$O$_3$ by the conventional solid-state reaction method, presented good dielectric properties when 0.2-0.8 at.% yttrium was used [5-9].

The wet chemical methods have attracted considerable attention for preparing oxide based materials with good control of the composition and microstructure. The most used chemical solution methods for preparing BaTiO$_3$ nanopowders are the hydrothermal method [10, 11], precipitation method [12, 13], sol-gel techniques [14-16] and sol-precipitation method [17, 18]. It is known that the structural and physical properties of BaTiO$_3$ prepared from solution are dependent on the choice of the precursors and the processing parameters [19, 20]. For example, inorganic salts (chlorides) sol-precipitation method and, alkoxide-hydroxide sol-precipitation method are used to prepare barium titanate [17, 18].

This paper propose an acetate-alkoxide sol-precipitation technique to prepare BaTiO$_3$, doped *in situ* with 0.5 at%Y, starting from barium acetate, titanium (IV) diisopropoxide bis-acetylacetonate and yttrium (III) butoxide. The as-obtained powder and ceramic are characterized as structure, morphology and dielectric properties.

2. Experimental

The sol-precipitation method presented here use moderate alkaline conditions (pH=9-10) as against the literature data (pH~13) [17, 18], in the aim to prepare a polymeric precipitate or gelatinous precipitate) with structure characteristic to the border product between gel and precipitate. By this reason, starting precursors which lead to a precipitate with organic structure were choice. Ba$_{0.995}$Y$_{0.005}$TiO$_3$ solid solution (BTY$_{0.005}$) was prepared by sol-precipitation method starting from barium acetate Ba(C$_2$H$_3$O$_2$)$_2$, (Aldrich), titanium (IV) diisopropoxide bis acetylacetonate ((CH$_3$)$_2$CHO)$_2$Ti(C$_5$H$_7$O$_2$)$_2$ (75 wt.% solution in 2-propanol), (Aldrich), and yttrium (III) butoxide (C$_4$H$_9$O)$_3$Y, (0.5M solution in toluene, 99.9+%), (Aldrich). This technique is based on the hydrolysis of the sol, followed by the precipitation of BTY$_{0.005}$ precursor from the alkaline sol. The distinct pH values of the precipitation (9-10) and of gelation (3.5-4) represent the main difference between the acetate-alkoxide sol-precipitation method involved in this work and the acetate-alkoxide sol-gel process used in previous paper [21].

A concentrated (1M) aqueous solution of barium acetate was prepared. Acetic acid glacial was added to the barium acetate solution, in molar ratio [(CH$_3$COO)$_2$Ba]sol1M:[CH$_3$COOH]=2:1. Titanium (IV) diisopropoxide bis acetylacetonate and yttrium (III) butoxide were mixed (molar ratio [Ti]:[Y]=1:0.005) while stirring the mixture at ~75 °C. Isopropanol and acetylacetone were added to the mixture of titanium and yttrium alkoxides in a proportion of 40/1. A ratio of 60%:40% = [isopropanol]:[acetylacetone] was used. The adequate mixed aqueous solutions of barium acetate and acetic acid were added gradually to the organic mixture containing the titanium and yttrium precursors. The sol obtained was kept under reflux with strong magnetic agitation at 75 °C for 2 hours. Distilled water and ammonium hydroxide were added gradually to the sol, in order to adjust the basicity of the mixture to pH=9-10 and to control the rate of the polymerization-precipitation

phenomenon. In the previous papers on the sol-precipitation [17, 18], NaOH/KOH aqueous solution were used to realize strong alkaline conditions (pH~13) necessary to precipitate the barium titanate ($BaTiO_3$). In this paper, ammonia was used to avoid the contamination of the precipitate with sodium or potassium ions. The precipitate was separated by filtration and carefully washed several times by deionized water, and then dried at 100 °C. The as-obtained powder was fired at various temperatures until 1300 °C and analyzed. The calcined powder at 1300 °C in air for 3 h was pressed into discs and sintered at 1250 °C to 1320 °C for 3 h in air.

The precipitate was analyzed by thermogravimetric (TG), differential thermogravimetric (DTG) and differential scanning calorimetry (DSC) methods using a TGA Instrument, model V5 1A 2000, DuPont, Wilmington, DE, at temperatures from 25 to 900 °C with a heating rate of 20 °C/min, in air. Infrared spectroscopy (IR) was also used for the characterization of the reaction product. The mixture of the precipitate powder and KBr was used for infrared spectroscopy studies using a Fourier transform infrared spectrometer FTIR (Model 8201 PC, Schimadzu Corp.). A phase analysis of the powders was performed by X-ray diffraction (XRD) and Raman spectroscopy. X-ray diffraction analysis was carried out using a Siemens D 5000 X-ray diffractometer. For powder diffraction, CuKα1 radiation (wavelength 1.5406) and a LiF crystal monochromator and Bragg-Brentano diffraction geometry were used. The data were acquired at 25 °C with a step-scan interval of 0.020 ° and a step time of 10 s. Raman spectrum was recorded at room-temperature using a spectrometer R−2001[TM]. The 785 nm line of a laser operating at 500 mW was used for excitation. The unpolarized radiation was collected with an instrumental resolution of 30 cm^{-1}. The morphology of the powders and ceramics was observed by field emission scanning electron microscopy (SEM, Philips XL 30). The density of the sintered ceramic was determined by using the Archimedes principle (in water). The temperature dependence of dielectric constant and dielectric losses were evaluated in the temperature range from 15 to 150 °C at 1 kHz by an Agilent 4263B LCR meter equipped with a thermostat. The electrical measurements were carried out in the metal-ferroelectric-metal (MFM) configuration where M is silver and F is the ferroelectric $BTY_{0.005}$. Silver paste, screen-printed on both surfaces and then heated at 650 °C for 30 min, was used as the electrodes.

3. Results and discussion

Thermal analyses results of $BTY_{0.005}$ precursor precipitate are presented in Fig. 1 and listed in Table 1.

The precipitate shows a mass loss of 9.270% up to 128 °C and another of 4.978% in the domain 128-250 °C. The thermal effects that accompany the mass loss indicated by the DSC curve, suggest processes as volatilisation of absorbed water on the grain surface, 2-propanol and acetic acid (thermal effect of 212.0 J/g, in the domain 85.96-160 °C) and, the evaporation of

acetylacetone (thermal effect of 74.32 J/g from 160 °C to 220 °C) respectively. The two endothermic peaks are centred at 131.26 °C and 166.98 °C, respectively.
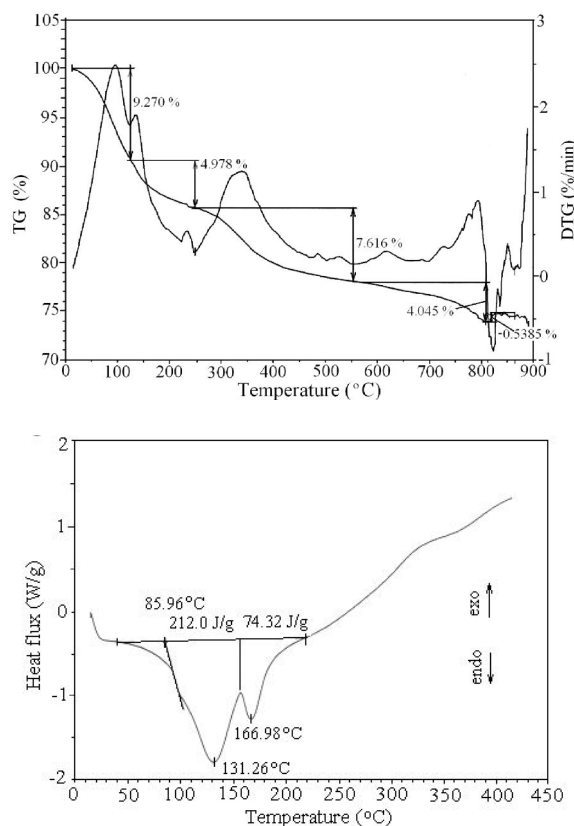

Fig. 1. Thermal analises results of $BTY_{0.005}$ precursor precipitate.

Table 1. Weight loss of $BTY_{0.005}$ precursor precipitate.

Temperature range, (°C)	Weight loss, (%)
25–128	9.270
128–250	4.978
250–550	7.616
550–811	4.045
811–865	- 0.5385

The next two steps of the volatile species loss take place with a smaller rate. A mass loss of 7.616% in the region 250-550 °C is due to the pyrolysis of the organic groups (exothermic peak). In the temperature range 550 °C to 811 °C occurs the formation of small amounts of barium carbonate ($BaCO_3$) by decomposition of $Ba(CH_3COO)_2$ [22]. Also, it can be observed a very small mass rise of the sample (0.6998 %) in the temperature domain 821.5-840.5 °C due to an oxidation process during apperance of $BaTiO_3$-Y_2O_3 solid solution.

FTIR spectrum of $BTY_{0.005}$ precursor precipitate dried at 100 °C (Fig. 2) shows transmission bands at 3380, 1625, 1575, 1450, 875 and 575 cm^{-1}. In general, lattice water

absorbs at 3550-3200 cm⁻¹ (antisymmetric and symmetric OH stretching) and at 1630-1600 cm⁻¹ (HOH bending) [23, 24]. The acetate complex present a strong asymmetrical stretching band ν(C=O) near 1575 cm⁻¹ and, a weaker, symmetrical stretching band ν(C-O) at 1450 cm⁻¹ [25, 26]. These bands mask the bands corresponding to acetylacetonate groups bonded to Ti (the bands centered at 1530 cm⁻¹ and 1590 cm⁻¹) [25].
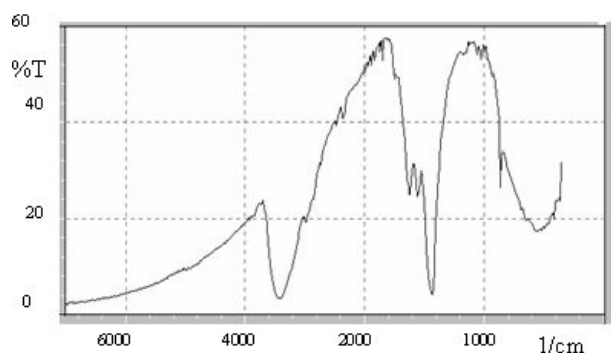

Fig. 2. FTIR spectrum of BTY_{0.005} precursor precipitate dried at 100 °C.

The bands due to OH bonded to titanium are centred at 1338 and 931 cm⁻¹ [27]. The low-frequency region of the spectrum (below 900 cm⁻¹) shows bands attributed to stretching metal-oxygen (Ti-O, Ti-O-Ti and, Ti-O-Pr^i) [25, 26]. The thermal analyses and infrared spectroscopy results indicated a polimeric precipitate with structure comprising organic groups (alcoxide, acetylacetonate and acetate) partially hydrolyzed.

The SEM micrograph of BTY$_{0.005}$ precursor sol-precipitate dried at 100 °C (Fig. 3), shows a microstructure consisting of grains with size of 100-200 nm. The grains are dispersed into a gelatinous matrix. This microstructure suggests a polimeric precipitate named also, gelatinous precipitate.
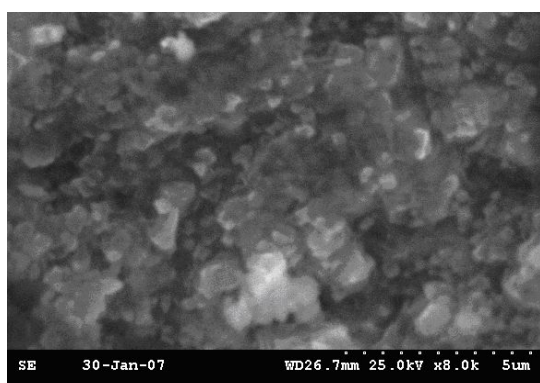

Fig. 3. SEM micrographs of BTY_{0.005} precursor precipitate, heated at 100 °C.

Fig. 4 shows the XRD patterns of (a) as-prepared BTY$_{0.005}$ precursor precipitate, (b) precipitate heated at 1300 °C for 3 h in air, and (c) BTY$_{0.005}$ ceramic sintered at 1300

°C for 3 h in air. XRD investigations on the precipitate resulted at pH=9-10 and dried at 100 °C have shown the witherite (orthorhombic BaCO₃) as phase present (Fig. 4(a)) [28]. Fan et al. [17], reported a cubic BaTiO₃ structure for the material prepared by sol-precipitation method in strong alkaline conditions (pH=13). BTY$_{0.005}$ powder crystallized on the tetragonal lattice of BaTiO₃ was obtained by firing the initial precipitate at temperatures 1300 °C for 3 h in air, Fig. 4(b), (Pattern 81-2202) [29].
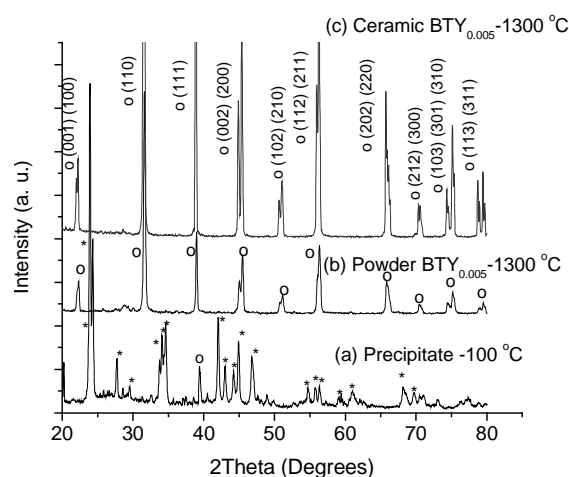

Fig. 4. XRD patterns (CuK_{α} radiation) of BTY_{0.005} precursor precipitate heated at 100 °C (a) and 1300 °C (b) and, pellets sintered at 1300 °C (c).

The tetragonal BaTiO₃ structure of BTY$_{0.005}$ powder is indicated also by the clear splitting of tetragonal peaks (002) and (200). The peaks belonging to tetragonal BaTiO₃ structure become stronger and sharper for the BTY$_{0.005}$ ceramic sintered at 1300 °C 3 h, as shown in Fig. 4(c).

The sharp peaks confirm the highly crystalline nature of the as-prepared BTY$_{0.005}$ powder and ceramic.

Fig. 5 shows the Raman spectrum of BTY$_{0.005}$ precursor precipitate fired at 1300 °C, recorded at room temperature.
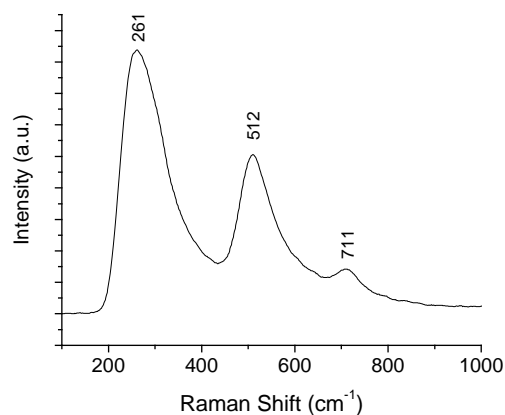

Fig. 5. Raman spectrum of BTY_{0.005} precursor precipitate fired at 1300 °C.

This spectrum presents peaks at about 261, 512 and 711 cm⁻¹ suggesting a crystalline material with the

structure of tetragonal $BaTiO_3$. For single-crystal $BaTiO_3$, Perry *et al.* [30] have been observed peaks of tetragonal $BaTiO_3$ at 269, 306, 516 and 720 cm^{-1}. In the Raman spectrum of $BTY_{0.005}$ precursor precipitate fired at 1300 °C, the two peaks at 269 and 306 cm^{-1} are masked by the large peak centred at 261 cm^{-1}. No other peaks have been detected. The Raman spectroscopy confirms that the precipitated $BTY_{0.005}$ precursor heated at 1300 °C is single phase.

To dielectric measurements, pellets of 12 mm in diameter and 2-3.5 mm thickness were obtained by uniaxial pressing of the $BTY_{0.005}$ powder, at 200 MPa. The ceramic discs were sintered at various temperatures in the range 1250 °C to 1320 °C. By sintering at 1320 °C for 3 h in air, the $BTY_{0.005}$ pellets shown a high deformation level due to start to melt and, at 1350 °C the pellets were fully molted.

The SEM micrographs of the pellets sintered at 1250 °C (a) and 1300 °C (b) for 3h in air (Fig. 6) shown well crystallized ceramics, with various grains size. Grains of 1-3 µm, with prismatic shapes, were observed for the ceramics sintered at 1250 °C (Fig. 6(a)).

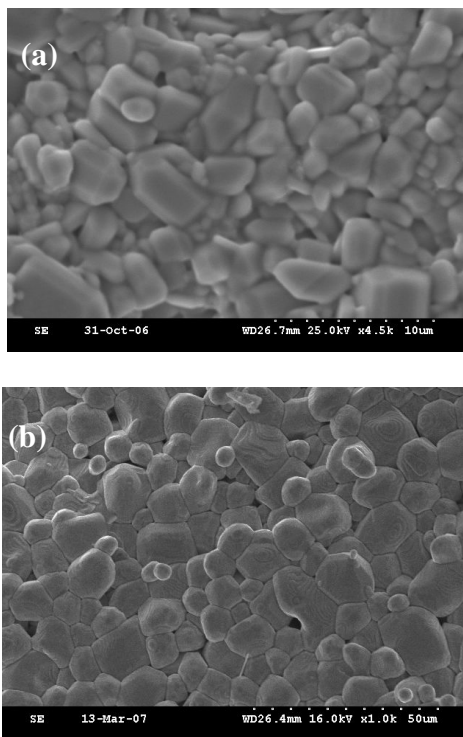*Fig. 6. SEM micrographs of the ceramic sintered at 1250 °C (a) and 1300 °C (b) for 3h in air.*

For the samples sintered at 1300 °C, 3 h there is a bimodal distribution in which grain sizes of 3-5 µm coexist with large grains (10-12 µm), as can be seen in Fig. 6(b). Some pores located in the triple points and at grain boundaries are observed. The apparent density of the sintered ceramic at temperature of 1300 °C was 92 % of the theoretical value of $BaTiO_3$.

The temperature dependence of dielectric constant and dielectric loss at 1 kHz, for $BTY_{0.005}$ solid solution sintered at 1300 °C for 3 h in air, is shown in Fig. 7.
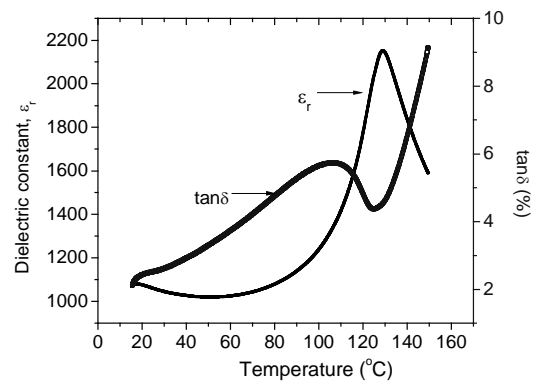

Fig. 7. Temperature dependence of dielectric constant (ε) and loss tangent (δ) of Y doped-BaTiO$_3$ ceramic at 1 KHz.

The dielectric constant and loss of $Ba_{1-x}Y_xTiO_3$, $x = 0.005$, measured at the Curie point temperature (125 °C) were 2152 and 4.54%, respectively. Obvious DC bias electric-field dependence of dielectric properties of $Ba_{0.995}Y_{0.005}TiO_3$ was observed. Figs.8-9 describe the dielectric response of Y doped-$BaTiO_3$ ceramic at room temperature (22 °C), under various DC bias electric-field.

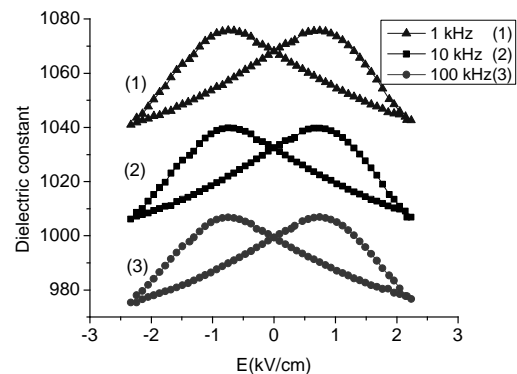*Fig. 8. Field dependence of dielectric constant of Y doped-BaTiO$_3$ ceramic at room temperature (22 °C) and, 1 KHz (1), 10 kHz (2) and 100 kHz (3).*

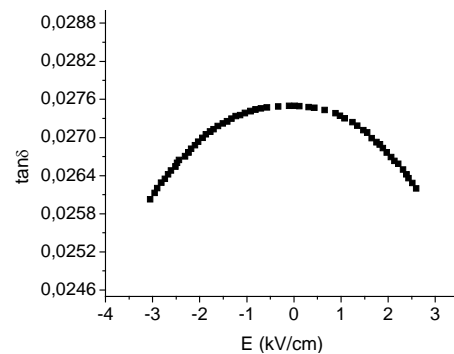The dielectric constant of Y doped-$BaTiO_3$ ceramic decreases as the frequency increases.

Fig. 9. Field dependence of dielectric loss of Y doped-BaTiO$_3$ ceramic at room temperature (22 °C) and 1 KHz.

The electric-field was applied in the following steps: (1) decreasing from -1000 V to zero, (2) increasing from zero to 1000 V, (3) decreasing from 1000V to zero, and (4) increasing from zero to -1000 V. With increasing the external DC bias electric-field from o to 1000 V, the dielectric constant decreases as well as the dielectric loss. In the region 0-2.6 kV/cm external DC bias electric-field, dielectric loss reached 5.45% indicating a small field dependence of dielectric loss of Y doped-BaTiO₃ ceramic at room temperature (22 °C) and 1 kHz (Fig.9).

4. Conclusions

I*n situ* Y doped BaTiO₃ was prepared by sol-precipitation in ammonia solution from barium acetate, titanium (IV) diisopropoxide bis acetylacetonate and yttrium (III) butoxide sol. Using moderate alkaline conditions (pH=9-10), a gelatinous precipitate precursor of $(Ba,Y)TiO_3$ was obtained. Single-crystal $Ba_{0.995}Y_{0.005}TiO_3$ perovskite phase with the structure of tetragonal BaTiO₃ was obtained after heating the precipitate at 1300 °C. The ceramic prepared from this powder shown good dielectric properties, comparable with literature data [6, 26] and, are suitable for dielectric device applications.

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