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INFLUENCE OF DIFFERENT SYNTHESIS ROUTES ON BARIUM TITANATE POWDER CHARACTERISTICS

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In this study, influence of synthesis route on compositional and morphological characteristics of barium titanate (BaTiO3- BT) powder was assessed. For this purpose, BT precursor mix was obtained by sol-gel method and then combined with classical thermal treatment – solid-state reaction, or hydrothermal method; for sol-gel method titanium iso-propoxide and barium acetate were used as precursors. The gelation time dependents on mixing order of the precursors. The X-ray diffraction and scanning electron microscopy have showed, in the case of combining sol-gel with hydrothermal method that a single mineralogical phase- BT results, as well as a mix of barium titanates in the case of combined sol-gel with classical method.

Keywords: sol-gel; hydrothermal method; barium titanate; mineralogical phases; morphological characteristics

1. Introduction

Barium titanate ($BaTiO_3$- BT) is a world-wide used material especially in the industry of electronics due to its electro-optical, piezoelectric, dielectric, and pyroelectric properties as well as its perovskite crystalline structure [1-15]. Below its Curie temperature it can have rhombohedral, orthorhombic, and tetragonal structures and above that it has a cubic structure. Up until today, the most used dielectrics for advanced ceramics capacitors are barium titanate ceramics [1-3].

Barium titanate is traditionally synthesised in powder form by calcinations at high temperatures of a mixture formed by titanium oxide and barium carbonate. This conventional method presents however some disadvantages due to the fact that mixture has a poor chemical homogeneity and, as a result, it favours the formation of large grains and also agglomerated crystallites [1, 5]. Thus, new, unconventional methods are required for obtaining this intensively used material, as e.g. sol-gel and/or hydrothermal method [16, 17].

The main objective of this paper is the synthesis of $BaTiO_3$ on a different route which allows to obtain a material that presents a higher purity, with smaller

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average grain size, at a lower thermal treatment temperature. One of those methods is related to the combination of two methods, sol-gel synthesis and hydrothermal treatment at a low temperature. The barium titanate presented in this study was obtained by association of those methods starting from barium acetate and tetrabutyltitanate. The resulted product presents good chemical homogeneity, fine particle size and most important high crystallinity.

2. Materials and methods

2.1. Materials

For obtaining the barium titanate precursor mixing by sol-gel method barium acetate ($Ba(CH_3COO)_2$, 98.5%, Sigma-Aldrich) and tetrabutyltitanate ($Ti(C_4H_9O)_4$, 99%, Sigma-Aldrich), dosing at molar ratio Ba:Ti=1:1 were used as reagents. Also, absolute ethanol (CH_3CH_2OH, >98%, Sigma-Aldrich) and acetic acid (CH_3COOH, 99.0%, Sigma-Aldrich) were used as solvents, and for the hydrothermal synthesis, potassium hydroxide (KOH, >98%, Sigma-Aldrich,) was employed as mineraliser.

The steps of sol-gel method were as follows:

(1) 55.32 g $Ba(CH_3COO)_2$ was dissolved in 100 ml CH_3COOH, 300 ml H_2O and 100 ml C_2H_5-OH; then 72.24 cm^3 $Ti(C_4H_9O)_4$ were added under continuous vigorous magnetic stirring until gelation (the gelation time was approx. 30 hours); at the end 25 ml H_2O was added;

(2) 55.32 g $Ba(CH_3COO)_2$ was dissolved in 100 ml CH_3COOH, 100 ml H_2O and 100 ml C_2H_5-OH; then 72.24 cm^3 $Ti(C_4H_9O)_4$ were added under continuous vigorous magnetic stirring for 30 min at 50 °C, with acidic pH (added 2-3 drops HNO_3); after that, 200 ml H_2O was added and under continuous vigorous magnetic stirring at 50 °C, until gelling (the gelation time was approx. 12hours); at the end 25 ml H_2O was added;

(3) 55.32 g $Ba(CH_3COO)_2$ was dissolved in 100 ml CH_3COOH, 100 ml H_2O; then 100 ml C_2H_5-OH was added under continuous magnetic stirring, at 50 °C; then, at the same temperature 72.24 cm^3 $Ti(C_4H_9O)_4$ was added under continuous vigorous magnetic stirring, with acidic pH (added 2-3 drops HNO_3); after that, 200 ml H_2O was added and under continuous vigorous magnetic stirring at 50 °C, until gelling (the gelation time was approx. 3 hours).

The (1), (2) and (3) sol-gel methods differ by the mixing order of precursors and the gelation time.

In all cases, after gelation process, maturation process took place for 24 hours at 50 °C, followed by gel drying at 80 °C for 24 hours. After that, the dried gel was cured using the following two methods:

- hydrothermal treatment (120 °C, 24 hours, 4M KOH aq. sol.; washed with ethanol and acetic acid and dried at 80 °C);

- classical thermal treatment by solid state reaction (1000 °C/3h; 1100 °C/3h; equilibrium cooling).

2.2. Methods

The mineralogical composition was assessed by X-ray diffraction (XRD); these analyses were performed in the range 2θ= 5-70 deg., using a diffractometer Shimadzu 6000 (λ = 1.5406 Å).

The morphological characteristics of powders were assessed by scanning electron microscopy (SEM) by means of Quanta Inspect F scanning electron microscope (1.2 nm resolution) coupled with EDX. Also, from these SEM images the average dimension of particles by statistical processing was assessed; for the statistical processing, fifty particle sizes were measured.

3. Results and discussion

3.1. Characterisation of dried gels

The X-ray diffraction analysis performed on dried gels – Fig. 1, showed the presence of the following main crystalline mineralogical phases: barium acetate ($Ba(CH_3COO)_2$; JCPDS 026-0131) and barium carbonate ($BaCO_3$; JCPDS 002-0364).

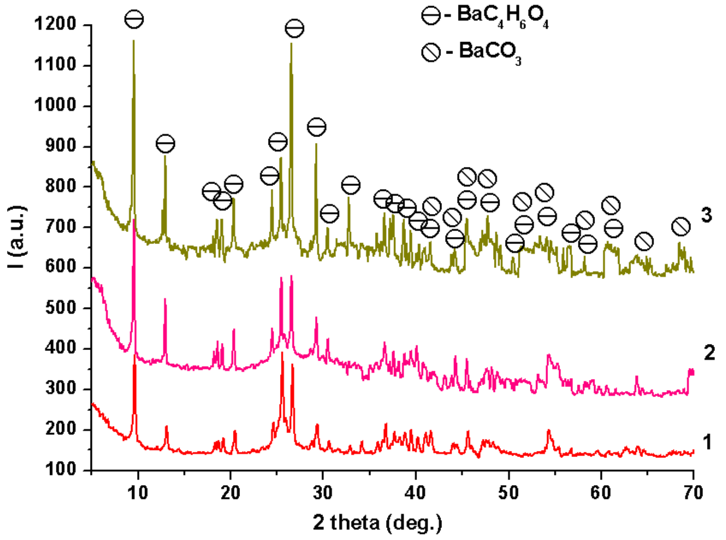

Fig. 1. X-ray diffraction patterns of dried gels obtained by route 1, 2 and 3

Their presence can be explained by partial recristallisation of barium acetate, and by carbonation with atmospheric carbon dioxide of barium hidroxide formed in wet environment, at barium carbonate.

3.2. Characterisation of gels treated by classical thermal treatment (solid state reaction)

The X-ray diffraction analysis of dried gels treated by solid state thermal treatment (classical) – Fig. 2, showed the presence of one of a mixture of barium titanates phases - $BaTiO_3$ (JCPDS 074-1963) and Ba_2TiO_4 (JCPDS 035-0813), at both treatment temperatures, in agreement with phase diagram [18]. From the point of view of crystallinity degree one can observe a low increase of this with increase of temperature.

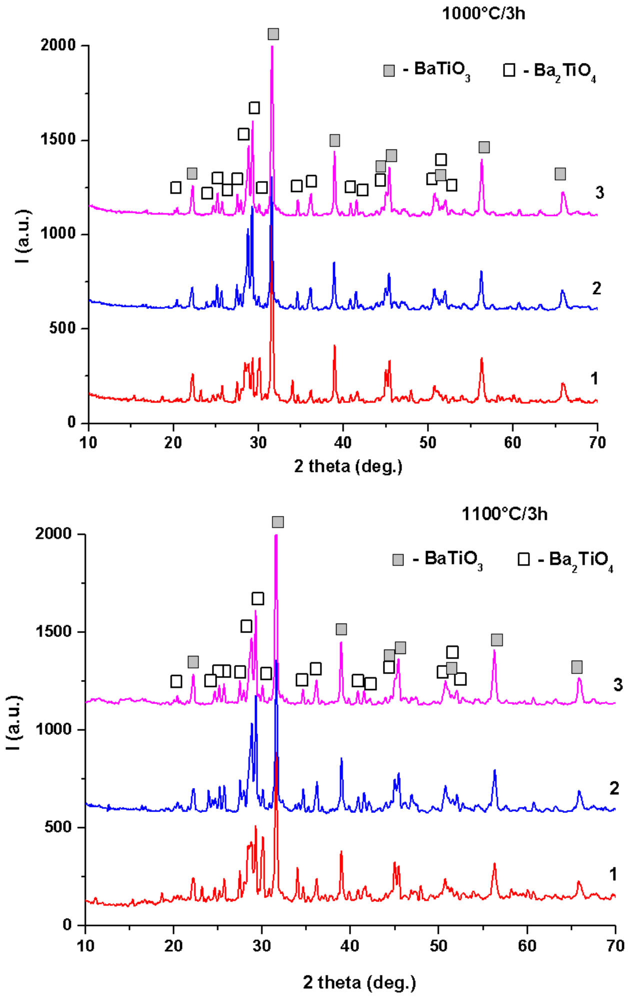

Fig. 2. X-ray diffraction patterns of dried gels obtained by route 1, 2 and 3 and thermal treated at 1000 °C/3h and 1100 °C/3h

Also, SEM images from Fig. 3 for dried gels treated by classical method at 1100°C for 3h showed the ceramic aggregates formed by crystals with different morphology - polyhedral and elongated particles, which suggest a mixture of barium titanate phases in correlation with the data obtained from XRD analyses.

The particles obtained by route 3 of syntheisis, have the lower average dimension; that can be explain probably by the different obtaining conditions of gels.

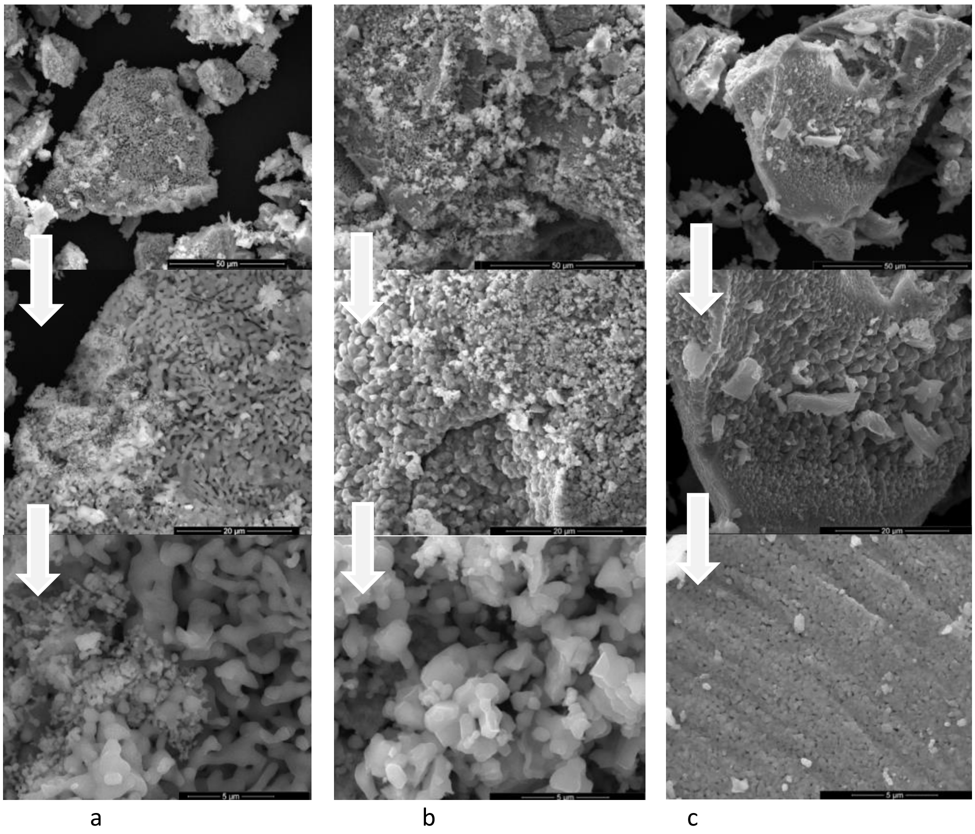

Fig. 3. Scanning electron microscopy images of dried gels thermal treated at 1100 °C/3h: a- route 1; b- route 2; c- route 3.

3.1. Characterisation of dried gels treated by hydrothermal treatment

X-ray diffraction analysis of dried gels treated by hydrothermal treatment – Fig. 4, showed the presence of barium titanate - $BaTiO_3$ (JCPDS 074-1963) as unique mineralogical phase; this could be due to a supercritical liquid environment. In the case of route 1, one can observe a very low intensity of the peaks for barium carbonate – $BaCO_3$ (JCPDS 002-0364).

The morphological characterisation of powders obtained by these three sol-gel routes and then hydrothermally treated (120 °C, 24 hours, 4M KOH aq. sol.), was performed by scanning electron microscopy (Fig. 5). SEM images showed for the gels obtained by route 1 - Fig. 5a, particles with almost polyhedral shape which are agglomerate in big aggregates. In case of routes 2 and 3 – Fig. 5 b, c, this polyhedral shape of particles is clearly identified; also, one can observe a decrease of agglomeration tendency of particles, especially for route 3.

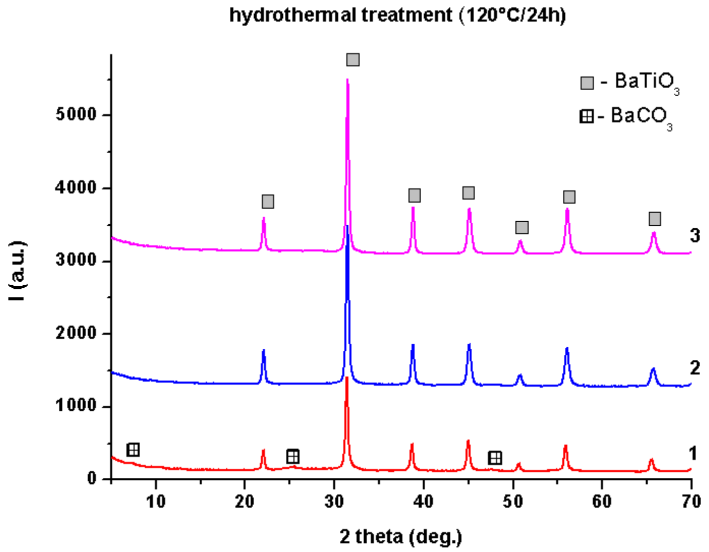

Fig. 4. X-ray diffraction patterns of dried gels treated by hydrothermal treatment (120 °C, 24 hours, 4M KOH aq. sol.)

This behavior can most likely be explained by the different conditions for obtaining gels.

By statistical analyses of SEM images from Fig. 5 (see the SEM images from the yellow squares) one can observe the particle dimension distribution of powders and their average size– Fig. 6. Thus, a good distribution (monomodal and uniform distribution) and smaller average size in case 3 were observed.

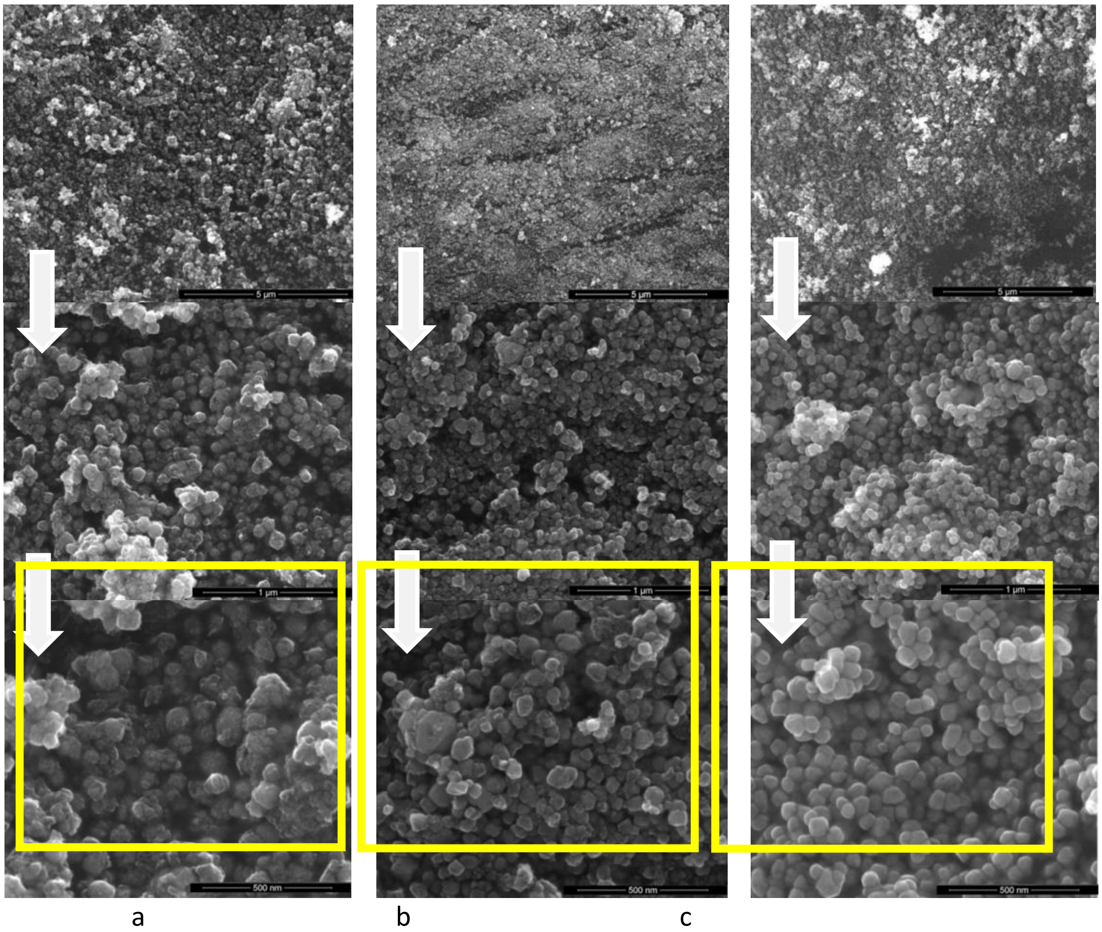

Fig. 5. Scanning electron microscopy images of dried gels treated by hydrothermal method (120 °C, 24 hours, 4M KOH aq. sol.): a- route 1; b- route 2; c- route 3.

4. Conclusions

To sum up, it can be concluded that:

i) the precursors mixing order in sol-gel methods, influences the gelation time; so, in the case of route 3 sol-gel method the addition of water, necessary for hydrolysis of metallic alkoxide increased the homogeneity of the mix, and lead to the decrease of gelation time and average size of particles;

ii) the type of thermal treatment applied in the last stage is of a significant importance, although the precursor mixture is obtained by the same sol-gel method; through this mineralogical composition and dispersion characteristics of the resulting material is influenced.

The classical thermal treatment (solid state reaction) of dried gels results in a powder with a multiphases composition (barium titanates phases mix - $BaTiO_3$ and Ba_2TiO_4); the hydrothermal treatment results in a powder formed by a single phase- barium titanate ($BaTiO_3$), this having an important role on final properties of the material in according to literature data [17].

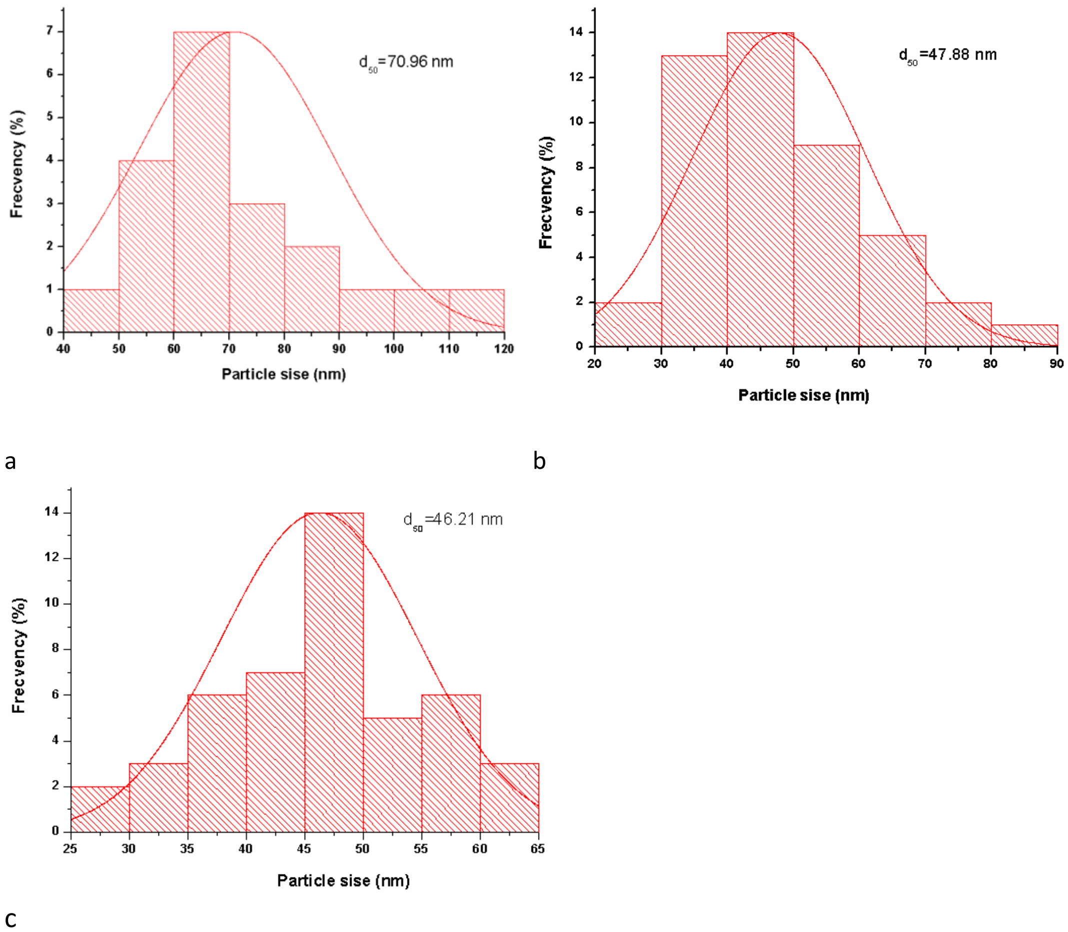

Fig. 6. Particle dimension distribution of dried gels treated by hydrothermal method (120 °C, 24 hours, 4M KOH aq. sol.): a- route 1; b- route 2; c- route 3.

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