Barium strontium titanate powders prepared by spray pyrolysis

G. Branković a,∗, Z. Branković b, M.S. Góes c, C.O. Paiva-Santos c, M. Cilense c, J.A. Varela c, E. Longo d

a Center for Multidisciplinary Studies of University of Belgrade, Kneza Vladoshe 1a, 11000 Belgrade, Serbia and Montenegro
b Department of General and Inorganic Chemistry, Faculty of Technology and Metallurgy, University of Belgrade, P.O. Box 494, 11001 Belgrade, Serbia and Montenegro
c Departamento de Físico-Química, Instituto de Química, UNESP, P.O. Box 353, CEP 14801-970 Araraquara, SP, Brazil
d Departamento de Química, Universidade Federal de São Carlos (UFSCar), CP 676, CEP 13565-905 São Carlos, SP, Brasil

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Abstract

Ultrasonic spray pyrolysis (SP) has been investigated for the production of the barium strontium titanate (BST) powders from the polymeric precursors. The processing parameters, such as flux of aerosol and temperature profile inside the furnace, were optimized to obtain single phase BST. The powders were characterized by the methods of X-ray diffraction analysis, SEM, EDS and TEM. The obtained powders were submicronic, consisting of spherical, polycrystalline particles, with internal nanocrystalline structure. Crystallite size of 10 nm, calculated using Rietveld refinement, is in a good agreement with results of HRTEM.

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1. Introduction

Barium titanate (BaTiO₃) and its related compounds have been used in the preparation of high dielectric capacitors, PTC resistors, ferroelectric memories, etc. Solid solution, ternary Ba₁₋ₓSrₓTiO₃, is ferroelectric, with tetragonal structure at room temperature for x<0.3 [1–3]. Curie temperature could be easily adjusted by changing of SrTiO₃ content in solid solution. Recently, it has been found that BST could be used for numerous applications such as tunable filters, oscillators, microwave phase shifters and many others [3,4]. The traditional method of preparation of BST by solid state reaction, from BaCO₃ or BaO, SrO and TiO₂, is not suitable for preparation of ceramics for high performance application because the material shows large particle size, nonhomogeneity and presence of impurities [4]. The possible solution of these problems is application of some chemical method in preparation of BST powders, for example, sol–gel, coprecipitation, hydrothermal or spray pyrolysis [5].

Spray pyrolysis is a promising technique for producing various materials in a wide range of composition, size and morphology. Powders and films can be successfully prepared [6]. Spray pyrolysis involves passing an aerosol of a precursor solution through a graded temperature reactor, in which the individual droplets are thermally decomposed to form oxide particles [5]. The aerosols may be generated by pneumatic or ultrasonic nebulizer. The ultrasonic nebulizer, which works at 1.7 MHz and 2.5 MHz could be used for aqueous solutions and the nebulizer which works at 850 kHz could be used for alcohol solutions. The ultrasonic nebulization has a narrow distribution of droplet diameter (1–10 μm, depending of type of piezo elements and type of solution). Several important processing parameters should be controlled to obtain a fine, single-phase powder. These are: carrier gas flow rate, time of passing an aerosol through the reactor, temperature profile inside the reactor and heating and cooling rates. Also, powder morphology depends on precursor type and a variety of physicochemical processes, such as reactant crystallization in the particle during solvent evaporation, chemical reaction in the particles and transport of gaseous reactants and products into and out of the particles [7].
In this work spray pyrolysis has been investigated for the production of the barium strontium titanate (BST) powders. It is very difficult to prepare stoichiometric compounds of titanium because titanium salts are mainly unstable; for example, TiCl₄, that is unstable at room temperature and could be already decomposed in atomizer before atomization, or Ti-isopropoxide, that hydrolyzes in air atmosphere. For that reason we prepared Ti-citrate as the precursor for the Ti ions. Other precursors were strontium acetate and barium acetate. The processing parameters were optimized to obtain single phase BST. The powders characterization confirms that powders are composed of spherical submicronic particles with internal nanocrystalline structure.

2. Experimental

The precursor solution for BST (Ba₀·₈Sr₀·₂TiO₃) was prepared starting from titanium citrate, barium acetate and strontium acetate. To form titanium citrate, titanium isopropoxide was dissolved in previously prepared solution of citric acid in ethylene glycol according to the following relation [8]:

$$\text{Ti-ion : citric acid : ethylene glycol} = 1:4:1.6.$$  

Stoichiometric amount of strontium and barium acetate were dissolved in water and two solutions were mixed together. The concentration of the final solution was 0.05 mol/dm³.

Schematic diagram of the equipment used in preparation of BST is shown in Fig. 1. Ultrasonic nebulizer of 2.5 MHz was used for aerosols generation. It is important to avoid the formation of carbonates during the synthesis of BST. It is well known that strontium and barium carbonates easily form in sol–gel processes when the organic precursor is used. This carbonate is very difficult to eliminate after thermal treatment. Since the carbonate forms at temperatures lower than temperature of BST formation it was necessary to perform fast heating of the aerosol. On the other hand, high heating rate can result in formation of porous particles or particles with volcanic structure. To obtain dense particles, without carbonate, it was necessary to optimize temperature and heating rate of thermal treatment. That was achieved by adjusting flux of the gas, aerosol flow rate and temperature of two chambers of the furnace.

After the complete optimization of parameters it was found that the best quality of the powder could be achieved under the following conditions:
- oxygen flux, 800 cm³/min;
- aerosol flow rate, 88 cm³/min;
- aerosol flow rate at the entrance of the furnace, 520 cm³/min;
- time of passing heating zone, 1 min;
- temperature at the first chamber of the furnace, 750 °C;
- temperature at the second chamber of the furnace, 600 °C.

The powder was characterized by the methods of X-ray diffraction analysis (XRD), scanning electron microscopy (SEM) with EDS analysis and transmission electron microscopy (TEM).

The X-ray diffraction data were obtained using a Rigaku® RINT2000 diffractometer (42 kV × 120 mA) with Cu kα radiation ($\lambda_{kα1} = 1.5405 \, \text{Å}, \, \lambda_{kα2} = 1.5443 \, \text{Å}$, $\lambda_{kα1}/\lambda_{kα2} = 0.5$), in the 2θ range between 20° and 100°, step 0.02° (2θ) with 6.0 s per point, using a divergence slit = 0.5 mm and receiving slit = 0.3 mm. The Rietveld refinements [9,10] were calculated using the program package General Structure Analysis System (GSAS) [11]. The peak profile function was modeled using a convolution of the Thompson-Cox-Hastings pseudo-Voigt [12] with the asymmetry function described by Finger et al. [13], which accounts for the asymmetry due to axial divergence. X-ray diffraction analysis with internal standard was performed to determine the percent of amorphous phase. SiO₂ was used as the internal standard. The powder mixture was prepared from 47.95 wt.% of BST and 52.05 wt.% of SiO₂.

3. Results and discussion

Results of X-ray diffraction analysis showed that almost single phase BST powder, with traces of carbonate (Fig. 2), was obtained under the optimal processing conditions. The large peak broadening suggests formation of small crystallites. Also, the high background around the (1 0 1) peak, which is the most intense one, indicates the existence of amorphous phase. This means that crystallization was not completed. Further, it was possible to observe change in color of the sample with time. After 60 days, it became slightly darker. As it could be seen in Fig. 2, there is one peak at 2θ = 24.36° that is noticeably smaller in diffractogram of sample recorded 3 days after synthesis in comparison to...
sample aged for 60 days. During the Rietveld refinements it was supposed that this peak belong to barium carbonate. The Fig. 3 shows the Rietveld plot for the BST with the SiO$_2$ internal standard. X-ray data was collected 60 days after synthesis of BST. The refined unit cell parameters confirmed this assumption. According to X-ray analysis the obtained powder contains Ba$_{0.8}$Sr$_{0.2}$TiO$_3$ phase (space group $P4\overline{mm}$) and small quantity ($\sim$1.5 wt.%) of BaCO$_3$ (space group $Pmcn$). Also, it contains approximately 42 wt.% of amorphous phase. Final values of lattice parameters, volume and density of BST powder, calculated by Rietveld refinement were the following: 

$$
\begin{align*}
    a &= b = 3.9897(3) \text{ Å}, \\
    c &= 4.0282(7) \text{ Å}, \\
    \alpha &= 90^\circ, \\
    V &= 64.12(1) \text{ Å}^3, \\
    \rho &= 5.783 \text{ g/cm}^3.
\end{align*}
$$

The unit cell parameters for the barium carbonate were: 

$$
\begin{align*}
    a &= b = 5.172(7) \text{ Å}, \\
    c &= 8.81(1) \text{ Å}, \\
    \alpha &= 90^\circ, \\
    \beta &= 90^\circ, \\
    \gamma &= 90^\circ.
\end{align*}
$$

Crystallites size of BST were \( \langle t \rangle_{||} = 9.8 \text{ nm} \) and \( \langle t \rangle_{\perp} = 10.8 \text{ nm} \). Table 1 contains the Rietveld agreement indexes after the BST refinements.

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<th>$R_{wp}$</th>
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<th>$R_F(Ba_{0.8}Sr_{0.2}TiO_3)$</th>
<th>$R_F(BaCO_3)$</th>
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<td></td>
<td>6.19%</td>
<td>4.76%</td>
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$R_{wp}$ is the weighted index, $S$ the goodness of fit ($S = \sqrt{\chi^2}$), $R_F$ is the structure factor index; all defined in Larson and Von Dreele [11].

SEM micrographs of the BST powders are shown at Fig. 4. The particles of BST are mainly smooth and spherical, with diameter in the interval from 100 nm up to 1 μm. There are no particle fragments or particles with volcanic structure. Some large particles are rather deformed, because they are formed from several smaller droplets. The smaller particles, which

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**Table 1**

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**Fig. 2.** X-ray diffractogram of the Ba$_{0.8}$Sr$_{0.2}$TiO$_3$ powder collected 3 days and 60 days after synthesis.

**Fig. 3.** Rietveld plot for the refinement of BST with internal standard. The superposed patterns are the observed and calculated ones. The bottom line is the residual observed-calculated pattern, the small vertical bars are the Bragg peak positions of each phase, as indicated in the figure.

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**Fig. 4.** SEM micrographs of the BST powder: (a) general look (EDS analysis was done on particles A–C) and (b) primary particles and some larger and deformed secondary particles.
are formed from only one droplet, are called “primary parti-
cles” (Fig. 4b). Impacts between droplets happened during a
transport to and through the heating zone and are responsi-
ble for formation of larger particles. The particles formed by
fusion of two or more droplets are called “secondary parti-
cles”. Probably deformed spheres (Fig. 4b) were obtained by
fusion of semi-dry droplets. EDS spectra of the three differ-
ent, randomly chosen particles showed that all particles have
the same composition (Fig. 5).

The morphology of the powders and densities of the parti-
cles are investigated comparing the experimental value of the
diameter with the calculated values. The theoretical diameter
could be calculated according the following equation:

\[ d = \left( \frac{cM_1}{\rho} \right)^{0.33} D_0, \]  

\[ D_0 = 0.34 \left( \frac{8\gamma}{\rho f^2} \right)^{0.33}, \]

where \( \gamma \) is superficial tension of the solution, approximately
same as of the water = 69.6 dyn/cm, \( \rho \) water density = 1 g/cm³
and \( f \) is frequency of the ultrasound.

In this way, the value of \( d_{cal} = 270 \) nm was obtained. This
is lower value than a mean diameter of primary particles from
the Fig. 4b indicating hollow structure and/or microporosity
of the particles. Nevertheless, a great part of the BST powder
consists of bigger particles. These secondary particles were
formed by coalescence of the smaller primary particles.

Transmission electron microscopy was done to determine
particle morphology, crystallite size, as well as homogeneity
at nanometer scale using EDS analysis. According to TEM
results, the particles are darker at particle borders, indicating
hollow structure (Fig. 6a). To investigate the crystallinity
the smallest particle from Fig. 6a was magnified in Fig. 6b. Under
magnification (Fig. 6b and c), it is possible to see that material
is not well crystalline in the whole particle and that there
are small crystallites sized 7–13 nm inside the particle with
diameter of 80 nm. Also, X-ray diffraction analysis showed
the presence of the amorphous phase and because of that
it was necessary to investigate a composition of this phase.
EDS analysis (Fig. 7) was performed at different points of the
figure to compare dark and bright parts at figure, parts with
and without crystal planes, as well as particle boundaries.
The spectra were almost identical at all observed points. This
means that both, crystalline and amorphous parts contain the
same, single phase BST. Obtained values of crystallite size,
as well as the observed amorphous phase, are in accordance with results of the Rietveld refinement.

Based on all results, it is possible to conclude that the obtained powder is consisted of polycrystalline particles, with hollow structure, and with significant amount of amorphous phase. This is a result of high heating rate, which was inevitable to suppress formation of carbonates.

4. Conclusions

Submicronic BST powder composed of spherical, polycrystalline particles was obtained by spray pyrolysis starting from titanium citrate and barium and strontium acetates. The powder has internal nanocrystalline structure, with great percent of amorphous phase, even more than 40%. The most of the particles were obtained by coalescence of the smaller particles.

According to the Rietveld refinement results the crystallite size was about 10 nm and that is consistent with the results of TEM. EDS analysis showed that all the particles are of the same composition, as well as that there is no change of composition throughout the particles.

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