



BaTiO₃ thick films obtained by tape casting from powders prepared by the oxalate route

Adelina Ianculescu^{1,*}, Sophie Guillemet-Fritsch², Bernard Durand²

¹*Polytechnics University of Bucharest, 1-7 Gh. Polizu, P.O. Box 12-134, District 1, 011061 Bucharest, Romania*

²*Centre Inter-Universitaire de Recherche de d'Ingénierie des Matériaux (CIRIMAT), Université Paul Sabatier, Route de Narbonne, 31062 Toulouse Cedex 04, France*

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Abstract

BaTiO₃ powders were prepared by co-precipitation via oxalate route. The size, morphology and particle size distribution of the oxalate powders have been optimized by the control of different synthesis parameters during the precipitation reaction (nature of salts, concentration of different solutions, aging time). The single phase BaTiO₃ oxide particles were obtained after a thermal decomposition of the as-synthesized powders at 850°C for 4 hours under air atmosphere. Oxide powders with a suitable specific surface area were selected in order to obtain thick films by the tape casting technique. The microstructure and dielectric properties of the thick films varied obviously depending on the deposition-calcination-sintering cycle used. A double deposition-calcination cycle followed by sintering, as well as a two step deposition-calcination-sintering procedure was used in order to improve the compactness and therefore, the dielectric behaviour. A higher dielectric constant value (~ 750) and lower dielectric losses (~ 2 %) were achieved at room temperature and at 1 kHz frequency for the dense, double-deposited film obtained after two deposition-calcination-sintering cycles. For this film, a superior value of the dielectric constant (~ 1100), almost frequency independent in the frequency range of 100 Hz – 10 kHz was gained also at the ferroelectric-paraelectric phase transition temperature of 130°C.

Keywords: BaTiO₃, co-precipitation, tape-casting, thick film, dielectric permittivity

I. Introduction

BaTiO₃ electronic ceramics are well-known for their high permittivity. BaTiO₃ compound is usually obtained by reaction of BaCO₃ with TiO₂. This traditional way of processing, i.e. the solid/solid method, offers the advantage of its simplicity. However, high temperatures ($T > 1000^\circ\text{C}$) are required to complete the reaction and prepare a single-phase material which has large particles, low surface area and uncontrolled microstructure. In order to overcome these disadvantages the low temperature, i.e. “soft chemistry” techniques have been developed. These methods permit to synthesize - at lower temperature - the same materials as the one observed at high temperature. Moreover, highly pure, submicronic, homogeneous and stoichio-

metric powders can be obtained. The advantages of using powders with reduced grain size to prepare thick films are increased specific area, improved reactivity and the possibility of lowering the sintering temperature. The chemical homogeneity, characterizing the powders prepared by low-temperature synthesis techniques, is a very important parameter for achieving reproducible properties.

The ongoing trend for higher integration in power electronic applications leads to the increase of the density of the components. While this operation can be achieved for power semiconductors, it is not the same for passive components. Obviously, their integration would be beneficial for the increase of reliability and thermal and electrical performances, and decrease of the costs while having an improved design. This technology may be achieved using a multilayer ceramic construction combining different functional ceramics together

* Corresponding author: tel: +40 214 023 984
 fax: +40 213 181 010,
 e-mail: a.ianculescu@rdslink.ro a_ianculescu@yahoo.com

in a 3D planar architecture [1–6]. Such approach needs multidisciplinary competence in circuit design, materials manufacturing and characterization. We show in this paper the first results obtained in this field. These results are presented and discussed in details from a physical and chemical point of view to an electrical one. The role played by the different constituents and the influence of the synthesis process on the electrical properties of the final products are also discussed.

II. Experimental

2.1. Powder and thick films preparation

The oxide powders were prepared by co-precipitation via oxalate route. The “precursor” powder (the mixed barium titanyl oxalate), was synthesized by pouring an aqueous solution of titanium chloride (TiCl_3) and barium chloride ($\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$) into an alcoholic solution of oxalic acid ($\text{H}_2\text{C}_2\text{O}_4$). Unlike the classical Clabauigh [7] procedure, when an aqueous solution of oxalic acid was used as precipitation agent, in this work the solvent was ethanol in order to increase the dielectric constant of the solution, leading to smaller particles [8]. The ageing time has to be long enough ($\sim 5\text{h } 30\text{ min}$) in order to complete the oxidation of the Ti^{3+} ions

into Ti^{4+} . The precipitated oxalate was separated from the liquid phase by centrifugation in a HERAUS Sepatech centrifuge for 10 min at 3500 rot/min, then washed several times with ethanol and dried at 100°C for 16 hours. The oxalate powder was annealed in air with a plateau of 4h 30 min at various temperatures in the temperature range of $750\text{--}1050^\circ\text{C}$, in order to select the powder with the optimal characteristics for thick film deposition. The synthesis flowchart of the BaTiO_3 powders is presented in Fig. 1.

The first step in depositing BaTiO_3 thick films was preparation of a suspension with optimal viscosity ($\eta \sim 2000\text{ cP}$) by mixing suitable amount of BaTiO_3 powder with some adequate organic components (solvent, dispersant and plasticizer). The as-prepared suspension is deposited in two successive layers by tape-casting on Pt electrode-coated alumina substrate. After the drying of the deposit at 80°C for 15 min, three different thermal cycles were tried in order to obtain superior dielectric characteristics. The first procedure consists of a calcination step of the deposit at 400°C , followed by sintering at 1200°C for 2 hours. The second procedure involves two successive deposition-calcination cycles followed by sintering in the same conditions and fi-

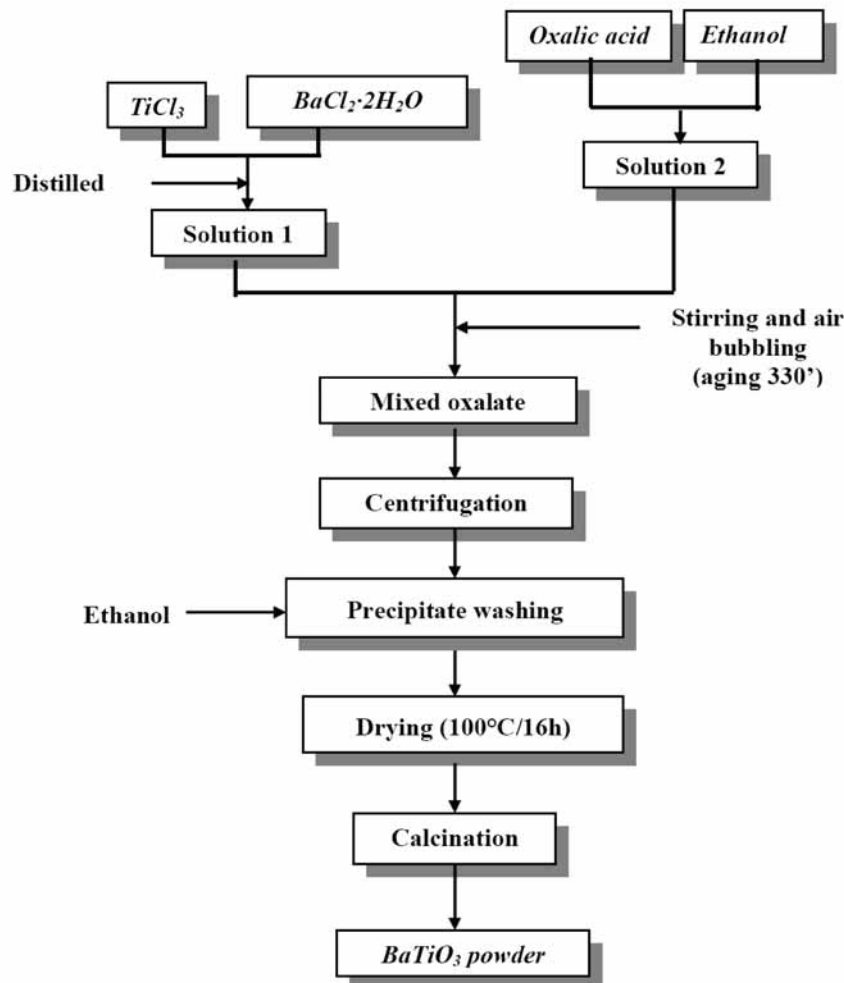


Figure 1. Synthesis flowchart for BaTiO_3 powders prepared by coprecipitation via oxalate route

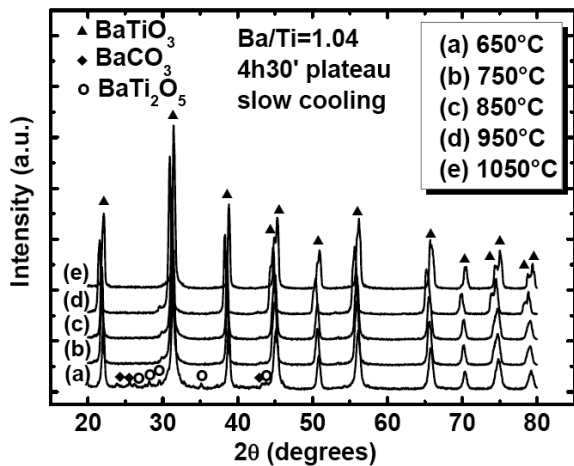


Figure 2. Room-temperature X-ray diffraction patterns for BaTiO_3 powders thermally treated in air for 4 h 30 min at various temperatures

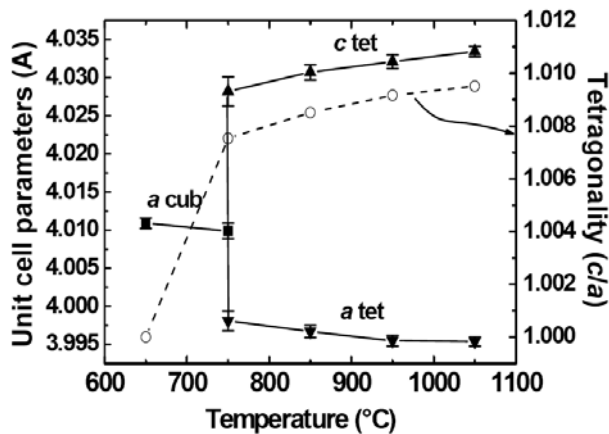


Figure 3. Evolution of the structural parameters (lattice constants and tetragonality) of BaTiO_3 powders versus the thermal treatment temperature

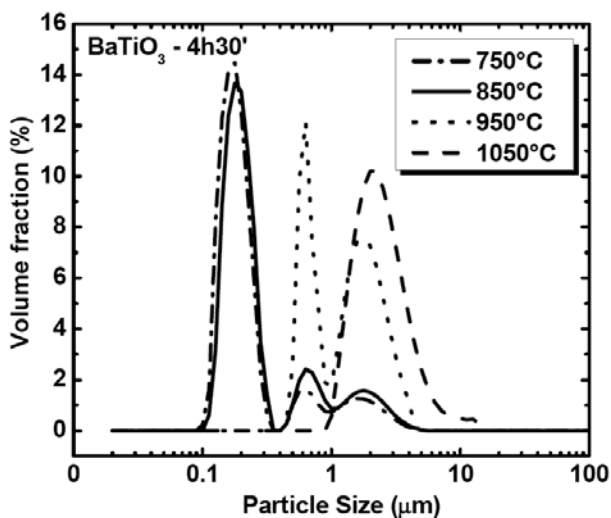


Figure 4. Particle size distribution for BaTiO_3 powders thermally treated in air for 4 h 30 min at various temperatures

nally the third procedure consists of two successive deposition-calcination-sintering cycles. After the deposition and thermal cycles, Ag top electrodes were deposited by screen-printing in order to perform dielectric measurements.

2.2. Powder and thick films characterization

The morphology of the oxide powders as well as the surface and cross-section morphology of the thick films were observed with a *JEOL JSM-6400* scanning electron microscope (SEM) and with a *JEOL 200CX* transmission electron microscope (TEM). Particle size distribution was investigated by means of Malvern 2000 particle size analyzer. The phase composition of both oxide powder and thick films was determined by X-ray diffraction analyses with a Bruker D500 diffractometer equipped with a Peltier effect counter and using Ni-filtered $\text{CuK}\alpha$ radiation ($\lambda = 0.15418$ nm) with a scan step increment of 0.03° and counting time of 1 s/step, for 2θ ranged between 20 – 80° . To estimate the structural characteristics (unit cell parameters), X-ray measurements were performed with a Seifert diffractometer, using a step increment of 0.02° with a counting time of 10 s/step for 2θ ranged between 20 – 120° .

The Ba/Ti ratio was measured by means of X-ray fluorescence using a Tracor X-Ray Spectrance 5000, in order to estimate the stoichiometry of the samples. The specific surface area was determined by the Brunauer, Emmet and Teller (BET) method using a Micrometrics Accusorb 2100^E.

Electrical measurements at various frequencies were performed on the thick films by using a Hewlett Packard 4284 A LCR-meter. Temperature dependence of the dielectric constant in the temperature range 20 – 200°C was determined from capacitance measurements performed on thick films placed in a small oven and heated in air. The bias dependence of the capacitance was investigated in order to estimate the ferroelectric state of the films. 1 V signal was used to measure the capacitance at 50 Hz as the bias voltage was ramped between -40 and $+40$ V.

III. Results and discussion

3.1. Characteristics of BaTiO_3 powders

The mixed oxalate precursor powder, obtained by using ethanol as solvent, has a specific surface area of 14 m^2/g and consists of small, uniform (in shape and size) and almost amorphous particles, with an average size of 70 – 80 nm. It has to be mentioned that for a given solvent there are also other processing factors, like aging time and synthesis temperature, which could affect the precursor particle size [9,10].

The thermal treatment parameters for the decomposition of the mixed barium titanyle oxalate precursor, mainly the thermal treatment temperature, can be tailored in order to obtain single phase, pure, fine, uni-

form and tetragonal oxide particles. Thus, powders synthesized in ethanol and annealed in air at different temperatures (maintaining a plateau of 4 h 30 min) exhibit different phase compositions, structures and particle sizes. From Figs. 2 and 3 one can see that in these conditions a minimal annealing temperature of 750°C is required to have pure and tetragonal barium titanate. For lower annealing temperatures (650–700°C), small amounts of secondary barium- or titanium-rich phases (BaCO_3 and BaTi_2O_7) were detected beside the major BaTiO_3 phase with pseudocubic symmetry, proving that the solid state reactions are not complete in this temperature range.

The annealing temperature strongly influenced the average particle size, which varied from ~ 60 nm (for the powder annealed at 650°C) and ~ 100 nm (for the powders thermally treated at 750 and 850°C) to $\sim 2 \mu\text{m}$ after annealing at 1050°C. The fine powders processed at lower temperatures exhibit a slight agglomeration tendency. It has to be mentioned also the bimodal particle distribution of BaTiO_3 powder, resulted after annealing at 950°C, which consists of finer particles of ~ 700 nm and larger particles with an average size of $\sim 1.8 \mu\text{m}$ (Fig. 4). The linear decrease of the specific surface area against the annealing temperature for the analyzed powders is presented in Fig. 5.

The SEM and TEM images presented in Figs. 6 and 7a show the uniform morphology of the BaTiO_3 powder obtained after annealing at 850°C for 4 h 30 min in static air atmosphere. The particle size of ~ 100 nm, estimated from the TEM image, is in good agreement with the average particle size determined by the particle size scattering analysis (Fig. 4). The HRTEM analysis coupled with SAED (selected area diffraction electron) investigation pointed out the single-crystal nature of the powder particles (Fig. 7b,c).

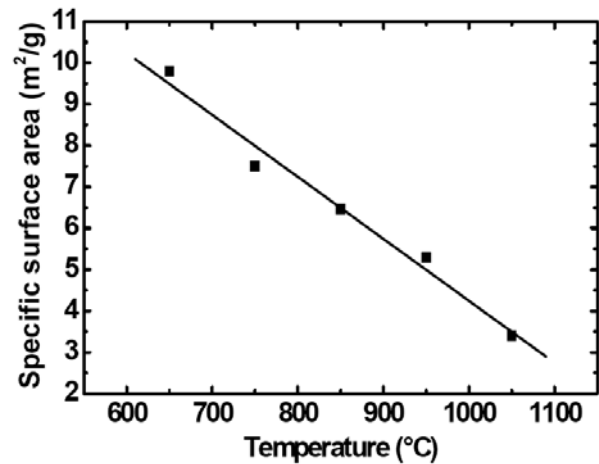


Figure 5. Evolution of the specific surface area of BaTiO_3 powders versus the thermal treatment temperature

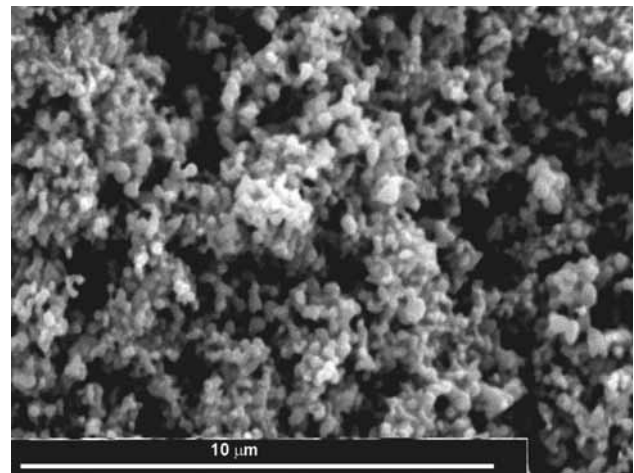


Figure 6. SEM image of BaTiO_3 powder thermally treated in air for 4 h 30 min at 850°C

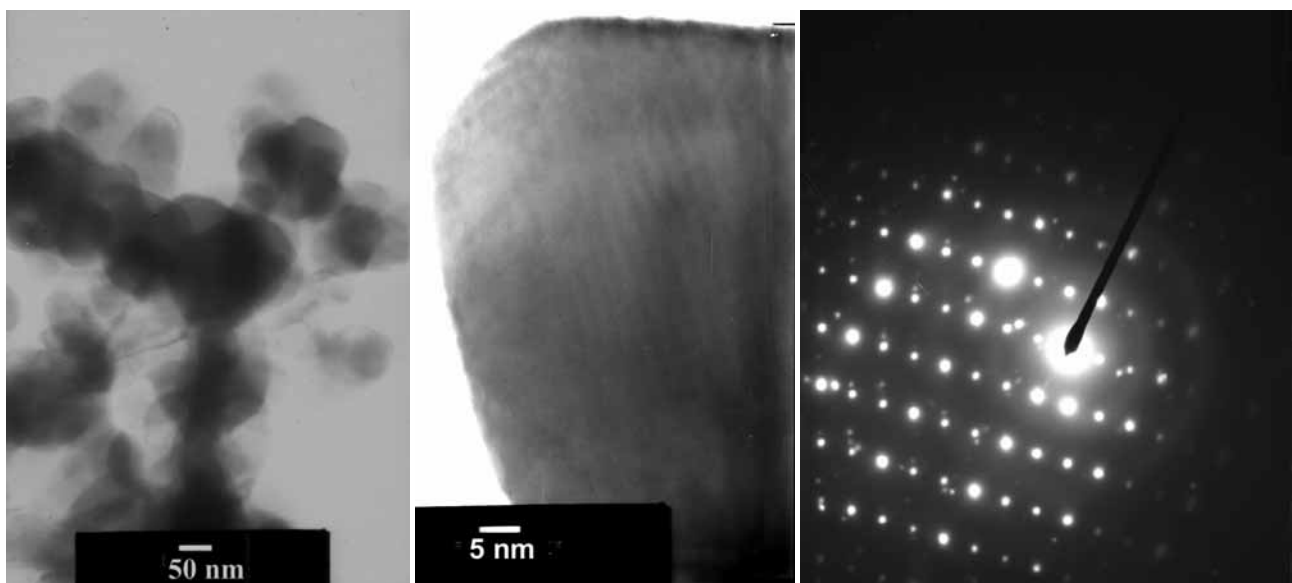


Figure 7. Morphology and crystallinity of BaTiO_3 powder synthesized by the oxalate route and thermally treated in air for 4 h 30 min at 850°C: (a) TEM image; (b) HRTEM image; (c) SAED pattern

3.2. Characteristics of BaTiO₃ thick films

In order to prepare homogeneous suspensions and, therefore, to deposit thick films with uniform thickness the single phase, stoichiometric BaTiO₃ powder with tetragonal structure, obtained after annealing in air at 850°C was considered as optimal. This powder had Ba/Ti ratio of 1.001 and specific surface area of ~ 6.5 m²/g. All thick films prepared by three different procedures already mentioned above, were single phase. Thus, in the X-ray diffraction pattern of the thick film deposited by the procedure no. 3, beside some peaks belonging to Al₂O₃ substrate and Ag electrode, only the well-crystallized perovskite BaTiO₃ phase was identified (Fig. 8).

Unlike the phase composition, the morphology and porosity of the BaTiO₃ thick films were strongly influenced by the type of the deposition-calcination-sintering cycle. Thus, concerning the surface morphology, the SEM images presented in Fig. 9a-c indicated a clear tendency towards more dense microstructure and decreased porosity starting from the procedure no. 1 (with two deposition steps followed by calcination and sintering) to the procedure no. 3 (by two deposition – calcination – sintering cycles). The films prepared by the procedure no. 1 and 2 show almost similar average grain size (of ~ 0.60 μm and 0.65 μm, respectively) (Fig. 9a,b). However, a higher compactness and a lower porosity were observed in the case of the thick film obtained by two different deposition – calcination cycles, followed by sintering (the procedure no. 2). Surprisingly, for the very compact and poreless thick film obtained by the procedure no. 3, a lower average grain size (of only 0.29 μm) was estimated on the film surface (Fig. 9c). In order to elucidate this aspect, further cross-section SEM investigations were performed. The cross-section SEM images showed that the transversal morphology of the BaTiO₃ thick films prepared by the procedure no. 1 and 2 was uniform (Fig. 10a,b, respectively), so we concluded

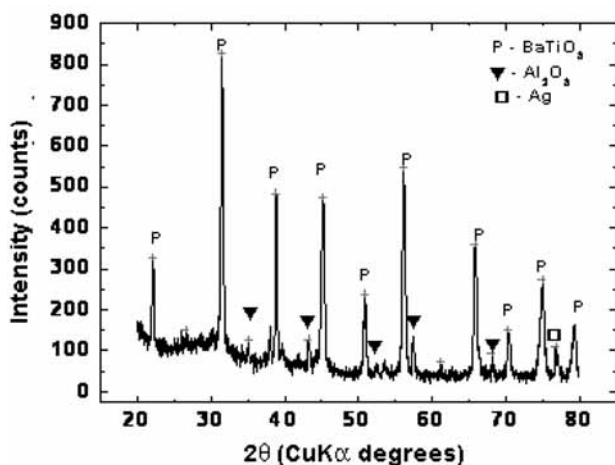
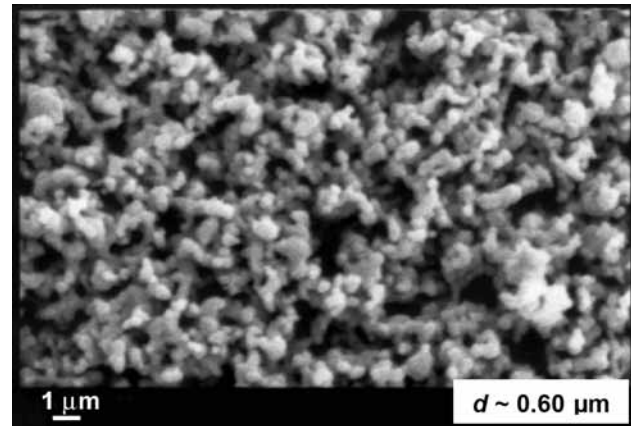
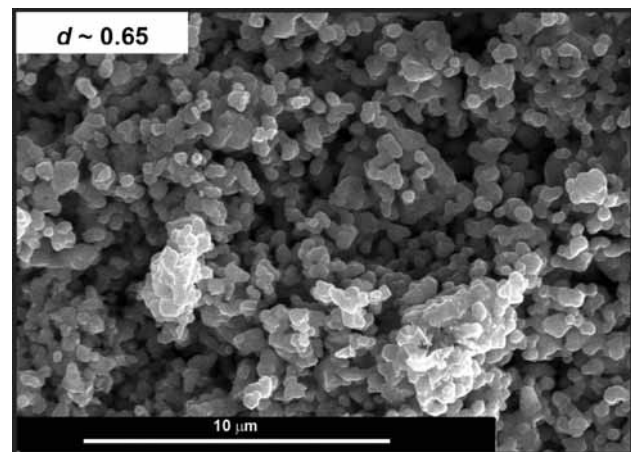


Figure 8. Room-temperature X-ray diffraction patterns for BaTiO₃ thick film prepared by procedure no. 3 (two deposition - calcination - sintering cycles)

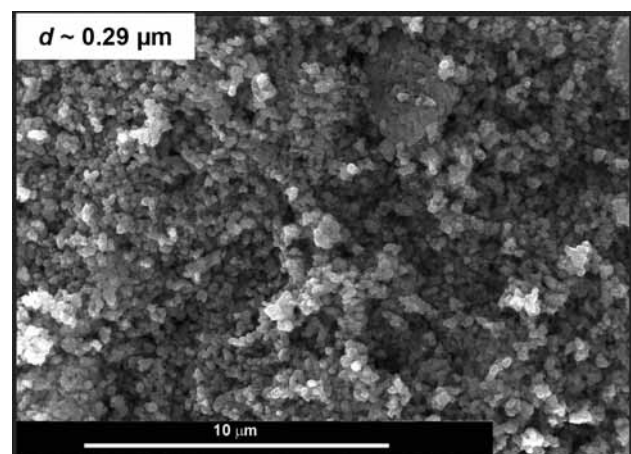
that the double calcination acts only in the sense of the porosity decrease and does not influence the average grain size. Unlike these samples, in the case of the BaTiO₃ thick films obtained by two successive deposition – calcination – sintering cycles (the procedure no. 3), a non-uniform transversal microstructure with a hetero-



a)



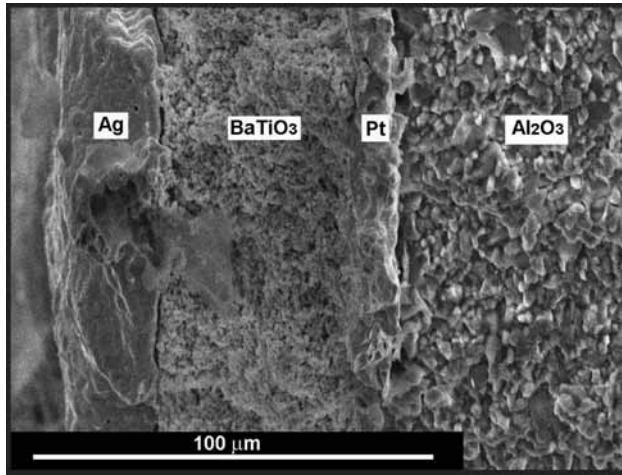
b)



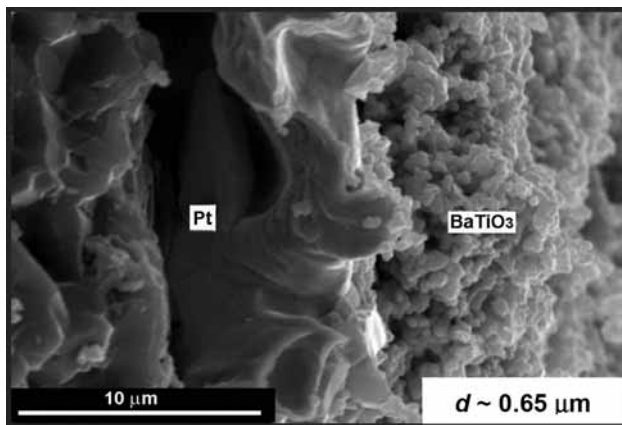
c)

Figure 9. Surface SEM images of the thick films prepared by: (a) procedure no. 1 (two deposition steps followed by calcination and sintering); (b) procedure no. 2 (two deposition - calcination cycles followed by sintering); (c) procedure no. 3 (two deposition - calcination - sintering cycles)

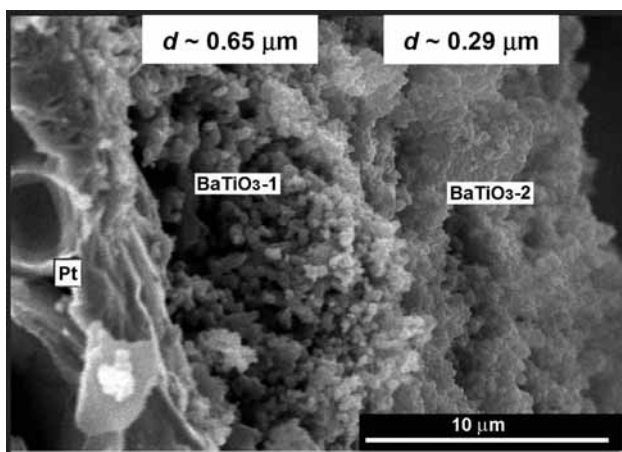
generality of the grain size across the film was pointed out. This microstructure induced by the double sintering process consists of two different layers clearly delimited by the different porosity and grain size, which decreased starting from the bottom layer to the top one (Fig. 10c). The presence of finer grains in the surface



a)



b)



c)

Figure 10. Cross-section SEM images of the thick films prepared by: (a) procedure no. 1 (two deposition steps followed by calcination and sintering); (b) procedure no. 2 (two deposition - calcination cycles followed by sintering); (c) procedure no. 3 (two deposition - calcination - sintering cycles)

layer of the thick film obtained by the procedure no. 3 suggests that the interface between the two deposits may act as an active, discontinuous nucleation surface for the crystallization of the second layer. In other words, the nucleation process is more favourable than the crystal growth, at least for the crystallization of the top deposit of this thick film. This feature was also noticed in the case of the multilayer BaTiO₃ thin films prepared by several *rf*-sputtering deposition – annealing cycles [11].

The higher compactness induced by the particular transversal microstructure of the thick film prepared by the procedure no. 3 determines the improvement of the dielectric behaviour. Thus, the room temperature dielectric losses at 1 kHz frequency decrease from ~ 25 % for sample 1 to 11 % for the sample 2 and to ~ 2 % for the sample 3. The evolution of the relative permittivity against the temperature at 1 kHz is quite similar for the samples 1 and 2 (Fig. 11). However, slightly higher values of the dielectric constant were obtained for the sample 2, mainly at the ferroelectric-paraelectric phase transition temperature ($\epsilon_r = 576$ for the sample 1 in comparison with $\epsilon_r = 652$ for the sample 2). At the same frequency, a sharper $\epsilon_r - T$ dependence with a well-marked maximum at the transition temperature and significantly higher values of the dielectric constant in whole temperature range were recorded for the thick film obtained by the procedure no. 3 (Fig. 11). In this case, the room temperature value of the dielectric permittivity is $\epsilon_r = 740$ and the relative permittivity at the transition temperature is $\epsilon_r \sim 1100$. No change in the value of the phase transition temperature ($T_c = 130^\circ\text{C}$) was noticed for three thick films analyzed in this work.

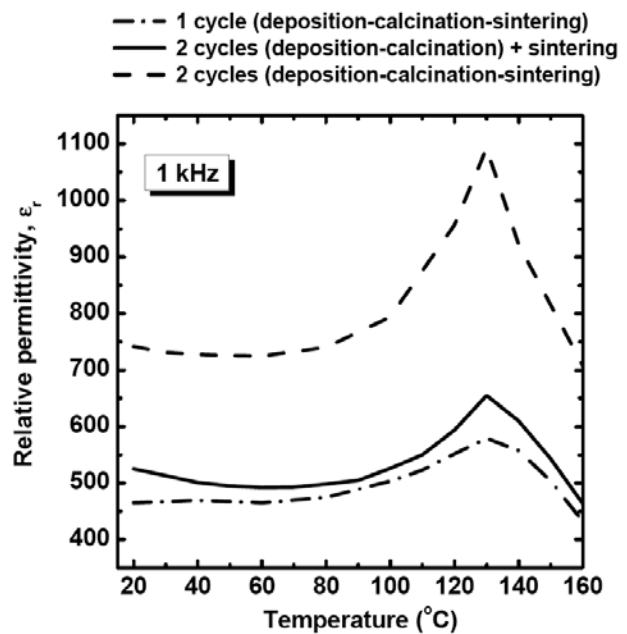


Figure 11. Dielectric constant versus temperature for the thick film prepared by the three mentioned procedures

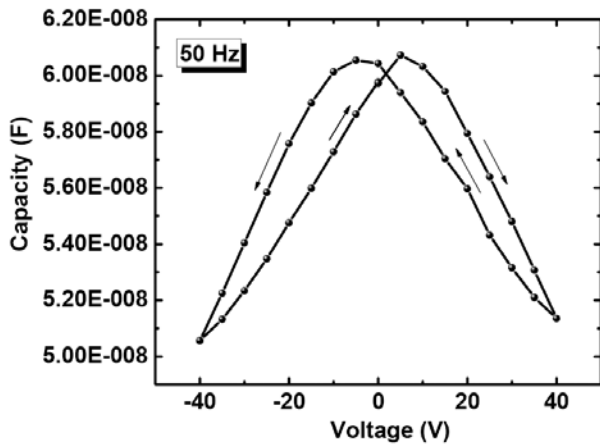


Figure 12. $C - V$ characteristic of the thick film prepared by the procedure no. 3 (two deposition – calcination – sintering cycles)

The capacitance variation with the dc bias is associated with the domain reorientation process [12]. Fig. 12 shows the voltage-dependent capacitance measured at 50 Hz for the $BaTiO_3$ thick film obtained by the procedure no. 3. A typical “butterfly” hysteresis in the $C - V$ plot, specific for the up- and down-ramped dc bias was recorded for this sample, indicating the ferroelectric nature of the thick film.

IV. Conclusions

Single phase, stoichiometric $BaTiO_3$ powders were prepared by co-precipitation via oxalate route after the thermal treatment of the mixed barium titanate oxalate precursor in air, at temperatures higher than 750°C , with 4 h 30 min plateau. Oxide powders with a suitable specific surface area were selected in order to obtain thick films by the tape casting technique. The microstructure and dielectric properties of the thick films varied obviously depending on deposition-calcination-sintering cycle used. A double deposition-calcination cycle followed by sintering, as well as two step deposition-calcination-sintering procedure were used in order to improve the compactness and therefore, dielectric behaviour. The double sintering process rather than the double calcination has a significant favourable effect on dielectric properties of the $BaTiO_3$ thick films. A higher dielectric constant value (of ~ 740) and lower dielectric losses (of $\sim 2\%$) were obtained at room temperature and at 1 kHz frequency for the dense, double-deposited film obtained after two deposition-calcination-sintering cycles. For this film, a superior value of the dielectric constant (of ~ 1100), almost frequency independent in the frequency range of 100 Hz – 10 kHz was also obtained at the ferroelectric-paraelectric phase transition temperature of 130°C .

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