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Doped Barium Titanate at Intermediate Stages of Synthesis of BTO

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This paper presents the results of synthesis and characterization of calcium 0doped nanocrystalline barium titanate powder with different concentration of doped elements ($(Ba_{1-x}Ca_x)$ TiO_3, were $x = 0$; 0.02; 0.06; 0.1; 0.16; 0.2), produced by oxalate route. Calcium additives were added on the surface the samples of semidecomposed barium titanil oxalate. For synthesis were used simultaneously decomposition of unstable barium, titanium compositions and calcium salts. The semidecomposed barium titanil oxalate and doped barium titanate characterization carried out by specific surface area measurements, TEM, X-Ray. It is experimentally shown that Ca^{2+} introduction reduces lattice parameter for samples that related with replacement of barium by calcium. Solubility of calcium in barium titanate nanopowders increase from 10 at % up to 16 at %. The second phase appears at 20 at %.

Keywords: Barium titanate, Material for dielectric layers, Doping, Calcium, Intermediate product, MLCC.

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1. INTRODUCTION

Traditionally, material for dielectric layers of capacitors are doped barium titanate with accordance EIA X7R specifications ($\Delta C/C$ = 15% from – 55 °C up to + 125 °C and dielectric loss tg $\delta \leq 2$ %). The one of most important problems in manufacturing of electronic components is miniaturization of the multilayer ceramic capacitors (MLCC). It could be achieved due to decreasing of the thickness of dielectric layer (0.5-1mkm) simultaneously with refining of grain size of dielectric [1]. Grain grows during sintering could be controlled on the one hand via optimization of the consolidation process, on the other hand - by doping of barium titanate. Grain size [2] and doping elements influence on temperature dependence relative permittivity. It is a hypothesis, that small addition of CaO could improve electrical properties of $BaTiO_3$ based ceramics. Thus, barium titanate ceramics doped with Ca^{2+} $(Ba_{1-x}Ca_x)$ TiO_3 have high dielectric constant ($\varepsilon = 3.000$ at $x = 0{,}06$) [3]. In addition, Ca-doped dielectrics show a time to failure of about 100 h under accelerated life test in comparison with only 9 h for the undoped barium titanate.

In the present paper we investigate partially decomposed barium titanyl oxalate (BTO), having porous granular structure of resin-like substance. Calcium was selected the dopant for these purposes.

Intermediate product of BTO decomposition represents porous granular structure of resin-like substance [4]. The granules do not contain crystalline phases inside and show channel network structure, which can be impregnated with soluble precursor of dopant. Final decomposition of all three batches of samples is suitable to form the doped barium titanate.

2. EXPERIMENTAL

The semidecomposed BTO (Ferro Electronic Components Corp.) was obtained by the calcinations at temperature up to 600 °C in quartz rotary reactor with air blowing.

Doped powder $(Ba_{1-x}$ $Ca_x)TiO_3$, where $x = 0$; 0.02; 0.06; 0.1; 0.16; 0.2 has been obtained by deposition of calcium chloride $CaCl_2$ and titanium chloride $TiCl_4$ of required concentration on earlier prepared samples of semidecomposed BTO by impregnation technique.

These samples were subjected to annealing up to 720 ºC in air. The samples for XRD analyses was annealing up to 1100 ºC. As a result, $(Ba_{1-x}$ $Ca_x)$ TiO_3 powder containing various concentrations of Ca^{2+} has been received.

Pore structure of samples was investigated by adsorption and structural method in ASAP 2000 M. It was measured adsorption/description isotherm of nitrogen in 77 K.

The XRD data were collected by Dron 3 diffractometer using Kα1 radiation from Cu anode. The morphology of the powders has been studied measuring the specific surface area (SSA) by adsorption using the BET isotherm and considering particle shape under TEM IEM-FXII.

By the data of XRD the lattice parameter was calculated to determine location of Ca^{2+} inside the lattice of $BaTiO_3$.

3. RESULTS AND DISCUSSION

Partially decomposed BTO do not contain phases inside and seems as porous granular structure (fig. 1). Mezoporous reactor is porous semidecomposed product of barium titanate synthesis from BTO. This structure consist pore size 30 Å (Fig. 2).

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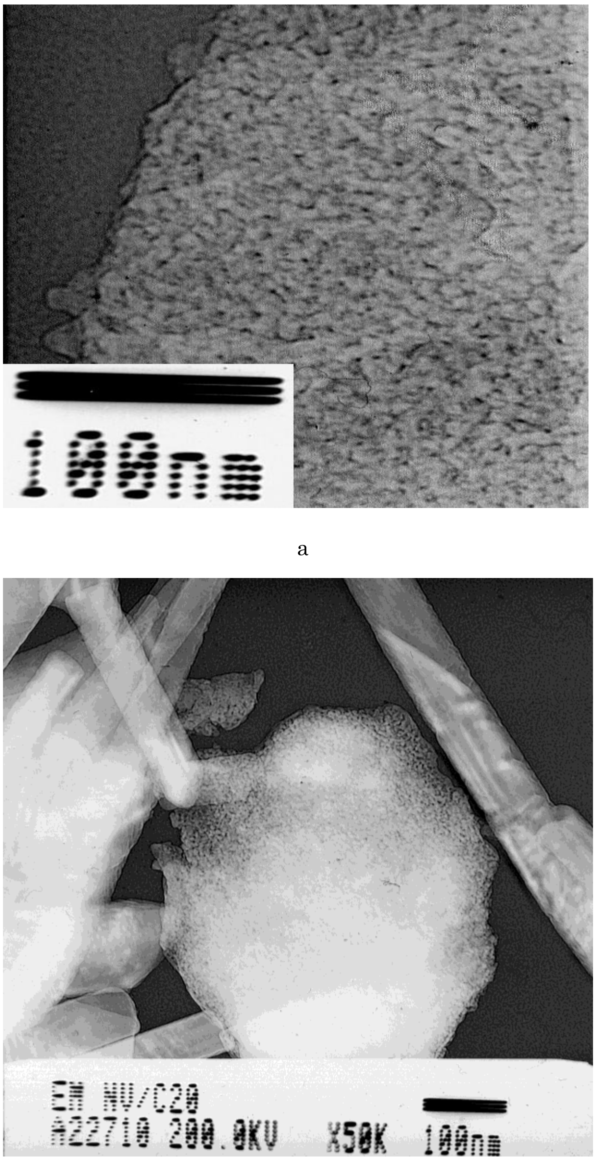

a

b

Fig. 1 – Porous granular structure undoped semidecomposed barium titanil oxalate (a,b)

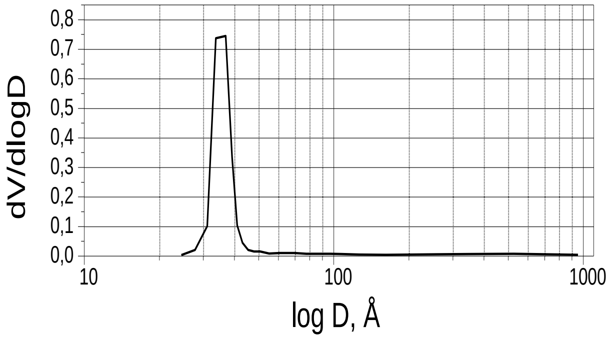

Fig. 2 – Pore size distribution for undoped semidecomposed barium titanil oxalate

This product from barium titanium oxalate is perfect mesoporous reactor for impregnation of doped elements. For example was used salt solution of calcium chloride (Fig. 3)

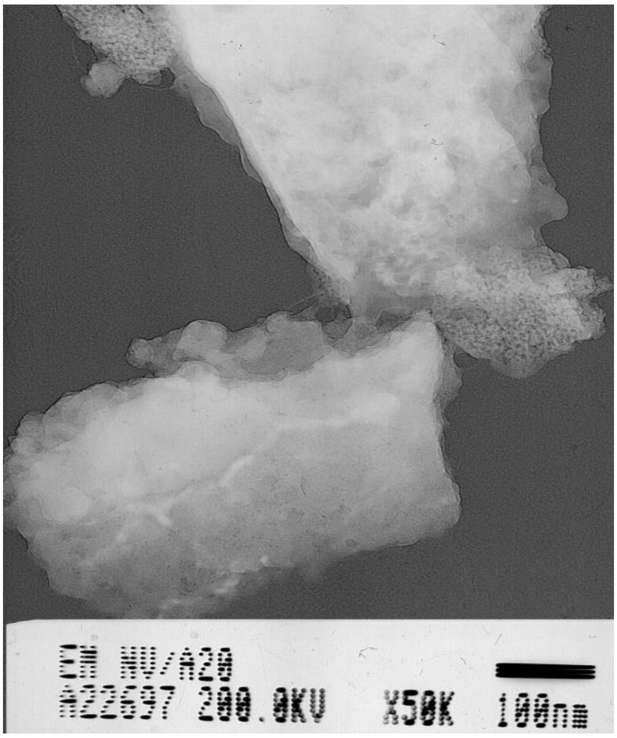

Fig. 3 – Porous granular structure with 20 at% content of calcium salts

Barium titanil oxalate with 20 at% content of calcium salts structure consist pore size 30 -40 Å (Fig. 4).

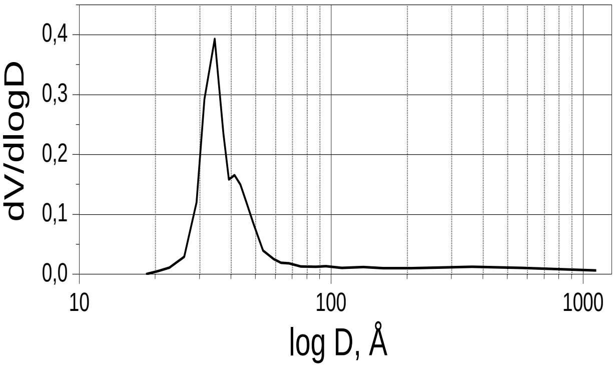

Fig. 4 – Pore size distribution for semidecomposed barium titanil oxalate with 20 at% content of calcium salts

High value of specific surface area 57 m^2/g was observed only for undoped semidecomposed barium titanil oxalate. Probable some pore of mesoporous reactor became covered of calcium salts and showed lower value. Specific surface area of impregnate semidecomposed barium titanil oxalate was like for all content of calcium salts and correspond 40 m^2/g.

After anneal at 720°C we take barium titanate doped by calcium.

Specific surface was 5-6 m^2/g (in accordance with particle size 210-190 nm) for the powder $(Ba_{1-x}Ca_x)$ TiO_3 doped on the intermediate stages of synthesis BTO and annealed up to 720 °C. Low value of specific surface can be explain double anneal of samples. It leads to agglomeration of powders.

Research of phase composition carried out after anneal at 1100°C of he barium titanate doped by calcium.

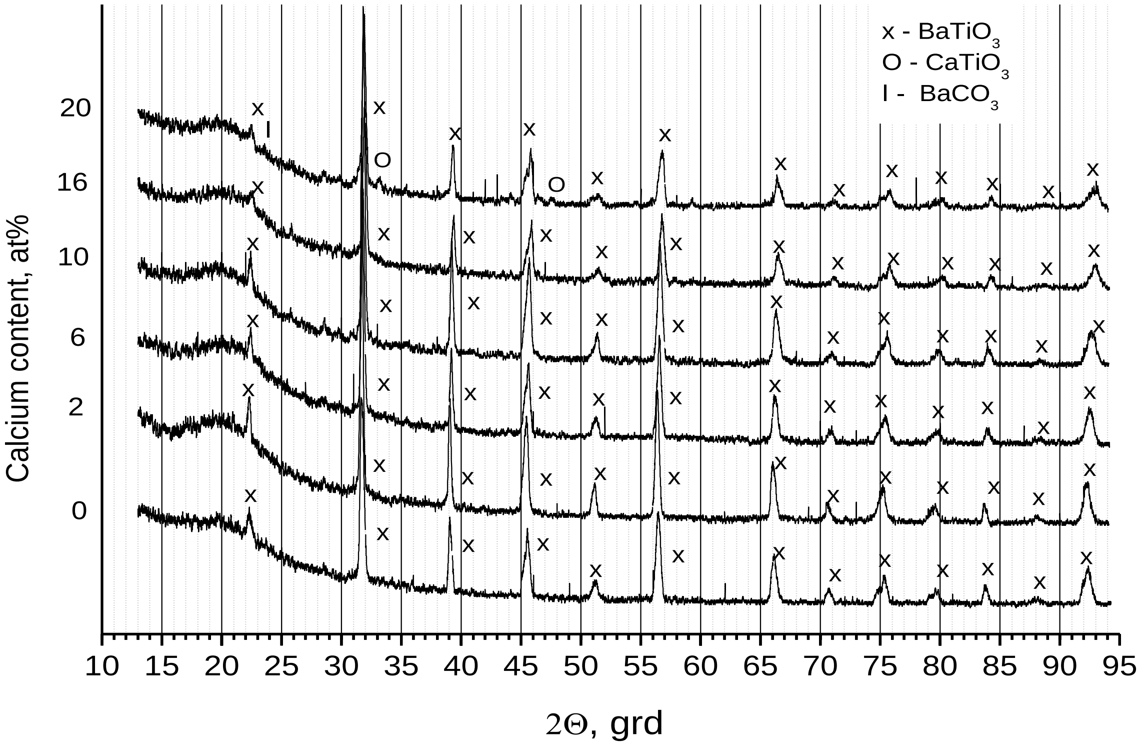

Fig. 5 – X-Ray patterns $(Ba_{1-x}Ca_x)TiO_3$ anneal at 1100 °C

Second phases not observed up to 16 at % (Fig. 5). In the XRD patterns the presence of the second phases $BaCO_3$ and $CaTiO_3$ peaks was observed for 20 at% content of calcium salts. It could be related with appearance of the carbonate phases during cooling process.

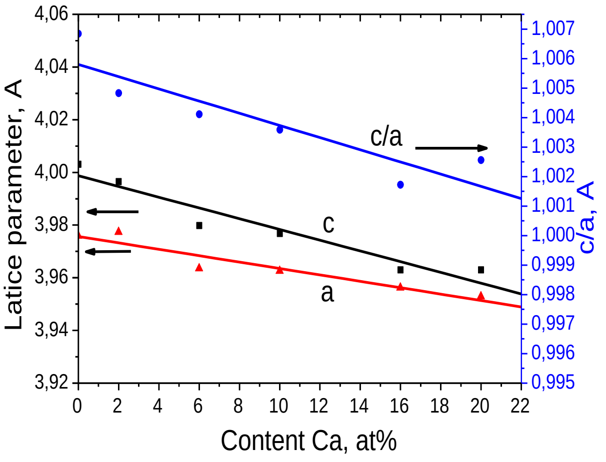

Fig. 6 – Latice parameter for the powder $(Ba_{1-x}Ca_x)$ TiO_3 with different content of calcium

The powder, during doping of intermediate product, contains some quantities of barium carbonate what related with chemical sorption of CO_2 on the intermediate components. The next annealing up to 1100 °C led to increasing of carbonates amount. Or we achieved solubility limit calcium in barium titanate lattice (16at % Ca at 1100 °C).

Values of lattice parameters ***a*** and ***c*** have been counted from XRD patterns. In Fig. 6 showed changes of parameters ***a*** and ***c*** for annealed powder $(Ba_{1\ x}Ca_x)$ TiO_3. The axis ***a*** and ***c*** for samples decreases. As ionic radius Ca^{2+} (1.04 Å) are less than ionic radius Ba^{2+} (1.38Å) that at Ca^{2+} replacement on the Ba^{2+} place, the lattice should decrease. This is observed for the $(Ba_{1-x}Ca_x)$ TiO_3 annealed powder.

4. CONCLUSIONS

New method of barium titanate doping was considered in this paper. It was carry out by impregnation technique of porous powders with specific surface 57 m^2/g, pore size 30 Å.

Second phases not observed up to 16 at %. Second phases $BaCO_3$ and $CaTiO_3$ peaks was observed for 20 at% content

It is experimentally shown: Ca^{2+} introduction reduces lattice parameter for samples that related with replacement of barium by calcium.

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