

# Synthesis and Dielectric Investigations of BaTiO<sub>3</sub> Obtained by Soft Chemistry Route

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**Abstract.** A new strategy for preparation of nano-sized barium titanate (BaTiO<sub>3</sub>) particles was applied by using: layered (tetramethyl)ammonium titanate, barium acetate and tetramethylammonium hydroxide. An addition of barium salt to aqueous layered titanate colloids leads to a precipitation phenomenon by which barium titanate precursor was obtained. The mechanism of this reaction is based on ions exchange which permits to incorporate barium ions into titanate layers. This was confirmed by comparison of broadband dielectric spectroscopy (BDS) data of layered (tetramethyl)ammonium titanate and barium titanate precursor.

**Key words:** precipitation, dielectric properties, sintering, X-ray diffraction analysis.

## I. INTRODUCTION

Materials with high dielectric permittivity are widely explored due to their importance in electronic components such as capacitors, gate dielectrics, memories or power-storage devices [1-2]. Barium titanate BaTiO<sub>3</sub> is a popular member of this material family which is characterized by high value of relative permittivity ( $\epsilon$ ), relatively low dielectric loss and exhibits ferroelectric and piezoelectric properties. Barium titanate with high value of dielectric permittivity is usually obtained by solid state reaction of BaCO<sub>3</sub>, or BaO, with TiO<sub>2</sub> and requires sintering at high temperatures [3]. Nowadays, trend of development is to obtain a ceramic material with excellent behavior via low sintering temperature. From this reason many different methods including e.g. chemical bath deposition or sol-gel processes are applied and products of their synthesis are carefully explored. These methods are classified as soft chemistry routes and have considerable advantages over conventional solid-state reactions, such as better compositional control, nano-sized precursor powders and lower crystallization temperature.

In this work a layered (tetramethyl)ammonium titanate (LTMAT) was used as a source of titanium. In aqueous environment it forms layered titanate colloids with nanosheet arrangements and exchangeable tetramethylammonium (TMA<sup>+</sup>) cations located in the interlayer. A presence of barium cations leads to ions exchange process by which BaTiO<sub>3</sub> precursor was obtained as a precipitate.

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## II. EXPERIMENTAL

**Synthesis.** The synthesis of BaTiO<sub>3</sub> precursor was conducted by mixing of two solutions. First one is a synthesis of the layered (tetramethyl)ammonium titanate which was conducted by means of the method described by Tomokazu Ohya et al. [4] starting from (tetraisopropoxy)titanium (TIPT) and (tetramethyl)ammonium hydroxide (TMAOH). The molar ratio of TMAOH/TIPT was  $R = 0.6$ . A precipitate of layered titanate was obtained by the addition of an excess of 2-propanol to the solution, separated by filtration, washed several times with 2-propanol to remove unreacted ammonium species and finally dried under vacuum. Transparent, aqueous layered titanate colloids (LTC) were prepared by dissolving 2.5 g of layered (tetramethyl)ammonium titanate in 250ml of water with addition of 1.2 ml TMAOH (25% wt.). The second one comprised of 5.45 g of barium acetate Ba(CH<sub>3</sub>COO)<sub>2</sub> • H<sub>2</sub>O mixed with 250 ml of water. Then, the both solutions was mixed and subjected to continuous stirring during 10 h at room temperature and further heating for 10h at temperature of 90°C. The resulting precipitate, being a BaTiO<sub>3</sub> precursor, was separated by centrifugation, washed several times with water to remove substrates which did not react, and finally dried in the vacuum. The total yield of dried powder was 3.53 g.

**Methods.** The X-ray diffraction patterns of samples were obtained using the X-Ray Siemens D 5000 X-ray diffractometer, which irradiated the samples with the monochromatic CuK<sub>α</sub>-doublet (40 kV, 30 mA). The diffraction curve was recorded in  $2\theta$ - steps of 0.03° with the counting time of 3 sec per step for all samples. All reference diffraction patterns were taken from the ICDD PDF-2 base.

The dielectric properties of materials under studies were investigated using a Novocontrol GmbH Concept 40 broadband dielectric spectrometer equipped with Quatro Cryosystem in the frequency range of: 10<sup>-1</sup>–10<sup>6</sup> Hz and in the temperature range: -80°C to 160°C (in steps of 10°C). In order to form a tablets required for dielectric measurements, the appropriate powders were pressed under the 13 000 LB load during 10 min. Three samples were tested by using broadband dielectric spectroscopy: (a) LTMAT, (b) BaTiO<sub>3</sub> precursor, (c) BaTiO<sub>3</sub> precursor subjected to sintering process at 1250° C for 4 h. In order to provide good contact between sample and external electrodes during electrical investigations by means of Novocontrol apparatus, the gold electrodes of the thickness equal 150 nm were deposited on the both sites of investigated tablets.

The obtained complex dielectric function ( $\epsilon^*$ ) has been measured:

$$\varepsilon^* = \varepsilon' - i\varepsilon'' \quad (1)$$

where:  $\varepsilon'$  and  $\varepsilon''$  are the real part and the imaginary or loss part, respectively.

### III. RESULTS AND DISCUSSION

A layered (tetramethyl)ammonium titanate was used as a source of titanium in presented method of  $\text{BaTiO}_3$  synthesis. The nanosheet organization in LTMAT was stated by Ohya et al. on a basis of XRD data and Raman spectra [4]. The lamellar arrangements of titanates is probable made of  $\text{TiO}_6$  sheets composed of zigzag ribbons of edge sharing  $\text{TiO}_6$  octahedra. Between interlamellar species a tetramethylammonium cations are placed, which provide a positive charges and assure electrostatic equilibrium for negative  $\text{TiO}_6$ . The  $\text{TMA}^+$  cations, located in the interlayer, can be exchange by other cations. The ion exchange mechanism in the titanates is not well explored. Valence, hardness and radius of cations are supposed to be the main factors affecting selectivity and exchange mechanism. An addition of barium acetate solution to layered titanate colloids caused a precipitation effect. This can be explained assuming a scenario, that layered structure was collapsed during  $\text{TMA}^+$  to  $\text{Ba}^{2+}$  ions exchange.

The broadband dielectric spectroscopy was chosen as a technique to assess an effectiveness of ions exchange process.

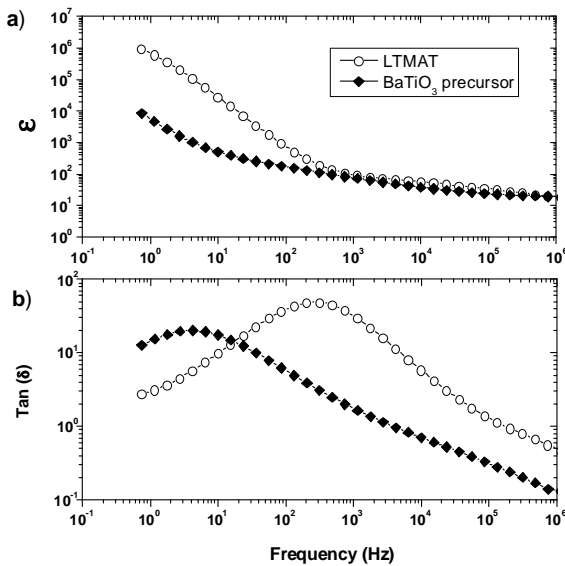


Fig. 1. Frequency dependence of : (a) dielectric permittivity and (b) loss tangent, measured for LTMAT and  $\text{BaTiO}_3$  precursor at  $70^\circ\text{C}$ .

In Fig. 1 the relative permittivity (Fig. 1a) and loss tangent (Fig. 1b) of LTMAT and  $\text{BaTiO}_3$  precursor vs. frequency are compared. One can notice that the  $\text{BaTiO}_3$  precursor exhibits significantly smaller permittivity from LTMAT in a frequency range of 1 to 500 Hz. This suggests smaller amounts of species which are able to move in electric field. At the same time the maximum observed for  $\text{BaTiO}_3$  precursor in loss tangent representation is shifted to lower frequencies as compared to layered (tetramethyl)ammonium titanate. Loss tangent representation reflects the energy that is dissipated in the form of heat due to dielectric polarization and/or by ions transfer connected to

dc conductivity of the material. Taking into account the chemical structure of LTMAT and  $\text{BaTiO}_3$  precursor, the maxima observed in Fig. 1b can be mainly attributed to the conductivity contributions. The shift of maximum position for  $\text{BaTiO}_3$  precursor to lower frequencies in loss tangent representation can be explained considering the stoichiometric nature of ion exchange. The replacement of monovalent TMA cation, coming from TMAOH which is classified as strong base, by divalent barium ion decreases the number of ions in the interlayer. This may lead to a shrinking of the basal spacing and by which  $\text{Ba}^{2+}$  cation will be immobilized and layer structure become more stable. A similar mechanism was proposed by Li et al. in the case of layered titanate nanostructures comprising sodium cations [5].

The  $\text{BaTiO}_3$  precursor, formed into a pellet shape, was further subjected to sintering process at  $1250^\circ\text{C}$  during 4 h. The obtained product was carefully investigated by Raman spectroscopy and XRD analysis. The XRD pattern (not presented data) confirm  $\text{BaTiO}_3$  formation with a small contamination of  $\text{BaTi}_2\text{O}_5$ . The BDS data (not presented here) exhibits a maximum between  $120 \div 130^\circ\text{C}$  in dielectric permittivity representation, which is a significance of Curie point corresponding to  $\text{BaTiO}_3$  structural transformation of the tetragonal form into cubic one, which is consistent with literature data.

### IV. CONCLUSIONS

It was confirmed that layered titanate colloid reacts in aqueous environment with barium ions leading to barium titanate precursor. The ion exchange mechanism was confirmed by broadband dielectric spectroscopy measurements. The applied sintering procedure leads to  $\text{BaTiO}_3$  which exhibits ferroelectric properties. A described method can be applied as an alternative, environmentally friendly synthetic process to produce ceramic materials.

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