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Prepared from Ultrasonically De-agglomerated BT Powders

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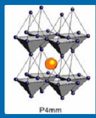
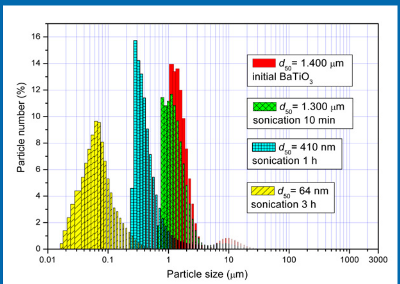
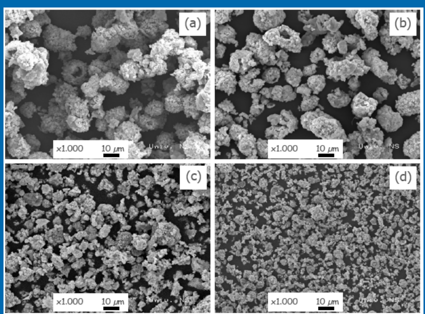


Powders preparation

Barium titanate (BT) powder, with average particle size of 1.4 μm, was synthesized by solid-state reaction. A high-intensity ultrasound irradiation (ultrasonication, using a direct-immersion titanium horn Sonics VCX– 750, 20 kHz, 750 W; 85% amplitude, 2s/1s pulse) was used to de-agglomerate micro-sized powder to nano-sized one. The crystal structure, crystallite size, morphology, particle size, particle size distribution, and specific surface area of the BT powder de-agglomerated for ultrasonication times of 0, 10, 60, and 180 min were determined. It was found that the particles size of the BT powder was influenced by ultrasonic treatment, while its tetragonal structure was maintained. Therefore, ultrasonic irradiation can be proposed as an environmental-friendly, economical, and effective tool for the de-agglomeration of barium titanate powders.



Particle size distributions of BT powders



Morphology of $BaTiO_3$ powders with average particle size of:
(a) 1.400 μm; (b) 1.300 μm; (c) 410 nm and (d) 64 nm.

Sintering at 1370 °C

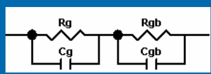
Impedance Spectroscopy

The shapes of Nyquist plots depend on temperature. At room temperature the shape of Nyquist plot is a straight line with a large slope indicating the insulating behavior of the samples. The *dc* resistance of the samples measured at room temperature was estimated to the range 2-72·10⁹ Ω. So, at room temperature, the impedance of the barium titanate ceramics is too high. The room temperature resistivity of BT ceramics depends mainly on the microstructural development associated with grain growth. Merely the data obtained above T_c, when the grain boundary resistance experience a drop by four order of magnitude (from 10^{10} to 10^6 Ω) provide more useful data.

To separate grain's and grain's boundary contributions, BT samples are heated up to 320 °C. The low frequency arc was not found at < 200 °C, which is due to the effect of electrode relaxation process overlapping with the grain boundary relaxation process. With increase in temperature (≥ 230 °C) impedance spectra for all samples contains two semicircles.

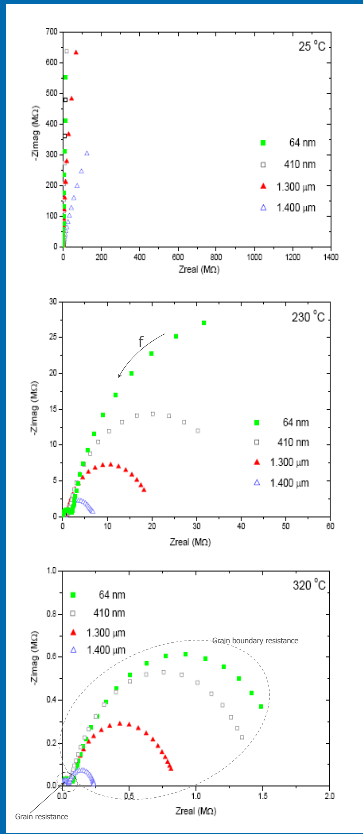
The amplitude of high frequency arc of the impedance spectra for BT samples having different grain sizes does not vary significantly with decreasing of grain size, and is ascribed to the grain resistance (R_g). The amplitude of low frequency arc increase with decreasing of grain size, and is ascribed to grain boundary resistance (R_{gb}).

Due to impedance data, the investigated BT ceramics can be modeled using an equivalent circuit consists of two parallel resistance-capacitance (RC) elements connected in series.

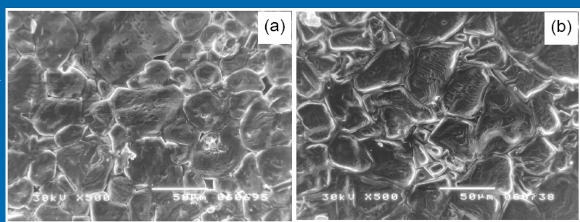


The impedance Z^* for above circuit

$$Z^* = [R_g^{-1} + j\omega C_g]^{-1} + [R_{gb}^{-1} + j\omega C_{gb}]^{-1}$$



Complex impedance plane Z at 25, 230, and 320 °C*



Microstructures of $BaTiO_3$ ceramics prepared from BT powders with average particle size of:
(a) 1.400 μm and (b) 64 nm.

Ceramics preparation

In order to investigate the influence of BT powder de-agglomeration on the shrinkage, microstructure and electrical properties of ceramics, the BT powders were uni-axially pressed into pellets (∅ 4 mm and *h*=2 mm) at 300 MPa. The average green density of the pellets was about 62% of theoretical density (T.D. 6.02 g/cm³). The samples were sintered in a heating microscope (E. Leitz, Wetzlar, Germany) in order to determine the sintering shrinkage. The experiments were performed in air up to 1370 °C, heating rate was 10 °C/min, the duration of the isothermal sintering was 2 h.

The electric conductivity of BT samples was investigated by an *ac* impedance spectroscopy over the frequency range of 1 Hz-100 kHz using a Gamry EIS300 Impedance Analyzer, in cooling from 320 to 25 °C; an applied voltage of 100 mV was used.

The microstructure of the sintered ceramics was studied on gold coated surfaces by scanning electron microscopy (SEM model JSM 5300) operating at 30 kV.

Transition parameters for BT samples sintered at 1370 °C

Average particle size (μm)	*c/a*	Crystallite size (hkl)	Crystallite size (nm)	Average grain size (μm)	$(\varepsilon_r)_{max}$	T_{max} (°C)	R_{tc} at 25 °C (GΩ)	R_g at 320 °C (kΩ)	R_{gb} at 320 °C (kΩ)
1.400	1.0077	**(002)** **(200)**	32(2) 69(2)	30	5924	108.2	2	50	187
1.300	1.0077	**(002)** **(200)**	31(2) 64(2)	30	6978	108.0	14	75	753
0.410	1.0077	**(002)** **(200)**	33(2) 64(2)	27	7518	106.6	56	46	937
0.064	1.0079	**(002)** **(200)**	29(2) 56(2)	13	7579	106.0	72	84	1650

Conclusion

- Barium titanate powder with an average particle size of 1.4 μm was synthesized by a solid state reaction. During different time periods of high-intensity ultrasonic de-agglomeration powders with the average particle size of 1.3 μm, 410 nm and 64 nm were prepared.
- XRD measurements show that the initial tetragonal crystal structure of $BaTiO_3$ has not been distorted by the ultrasonic de-agglomeration. Average crystallite size has not been changed after prolonged irradiation.
- Reduction of the average particle size of the initial powder leads to a reduction of the average grain size of the sintered ceramics.
- Microstructure of barium titanate ceramics significantly influences their electrical properties. Reduce of the average grain size and increase of density promotes an increase in both dielectric constant and grain boundary resistivity.
- The powder's average particle size and/or the size of agglomerates have limiting influence on the grain size in the final ceramic. The electrical characteristics of barium titanate ceramics primary depend on the average grain size of the sintered samples. All investigated properties, including dielectric constant and grain boundaries resistivity, increase with decreasing of the average grain size. It can be emphasized that the electrical characteristics of the sintered ceramics are very sensitive to ceramic density, grain size and to shape of grain boundaries. Therefore, fine-particles BT powder is desirable for achieving a higher grain boundary resistivity.
- Impedance spectroscopy shows that the electrical behavior of grain boundaries depended on the ceramic's microstructure and consequently on the starting powder's average particle size.
- The high-intensity ultrasound irradiation enables improvement of physical characteristic of barium titanate powder prepared by solid state reaction, producing uniform nanometer-sized powder suitable for preparation of dense ceramics with good electrical properties.