YUCOMAT 20

Characterization of Barium Titanate Ceramics by Impedance Spectroscopy

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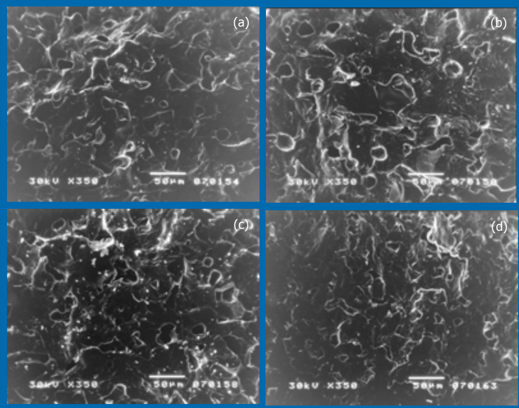
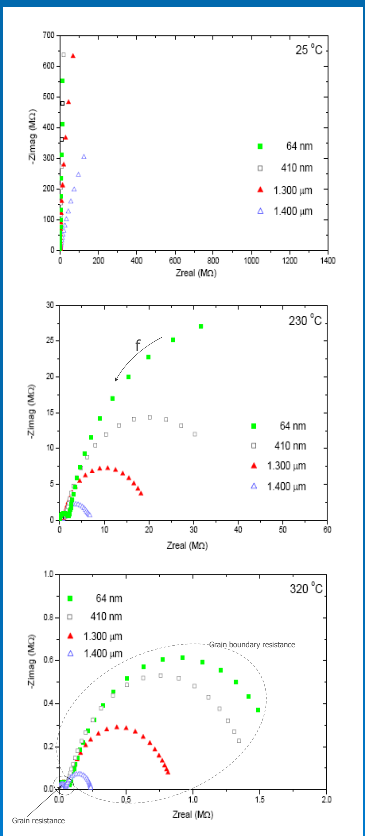
Here, we report the results of electrical properties of barium titanate ($BaTiO_3$) sintered ceramics. The ceramics were prepared from four different particle-sized $BaTiO_3$ powders, and sintered at 1370 °C for 2h. The electrical properties of sintered ceramics were investigated by *ac* impedance spectroscopy over the ranges 25-320 °C and 1 Hz-100 kHz. Result are compared with those obtained from fixed frequency measurements, at 1 kHz. Impedance spectroscopic data obtained at solids are often interpreted in terms of serial equivalent circuit models. In these models each relaxation process in a spectrum is usually related to exactly one transport or relaxation process, i.e. to one sample region (e.g. bulk, grain boundary, and electrode) or reaction step. Here, an impedance model for the grain boundary in $BaTiO_3$ ceramics is proposed. The grain boundary is ferroelectric, similar to the grains, but its impedance is modified by either air gaps or high-impedance electrical inhomogeneity in the region of the necks between the grains. Finally, the grain size of barium titanate ceramics was correlated to the ceramics electrical properties.



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

Microstructure was observed on fracture surfaces of ceramics sintered at 1370 °C for 2 h.



Complex impedance plane Z* at 25, 230, and 320 °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 (*dc* – frequency-independent resistance) of the samples measured at room temperature may be 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.

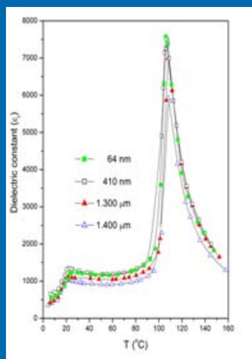
To separate grain's and grain's boundary contributions, BT samples are heated up to 320 °C. The low frequency arc was not found at < 200 °C, which is due to the effect of electrode relaxation process overlapping with the grain boundary relaxation process. With increase in temperature (≥ 230 °C) impedance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

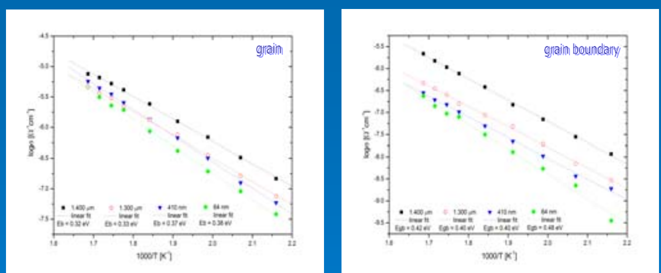
The impedance Z^* for this circuit

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



Permittivity vs T at 1 kHz

Activation Energy



Arrhenius plot of grain and grain boundary conductivity data of BT samples sintered at 1370 °C in air

Arrhenius equation

$$\sigma=\sigma_o \exp(-E_a/kT)$$

Bulk and grain boundary conductivity data obeyed the Arrhenius law with similar bulk and grain boundary activation energies for all samples.

Summary of transition parameters for $BaTiO_3$ 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)	E_g^a (eV)	E_{gb}^a (eV)
1.400	1.0077	**(002)** **(200)**	32(2) 69(2)	30	5924	108.2	2	50	187	0.32	0.42
1.300	1.0077	**(002)** **(200)**	31(2) 64(2)	30	6978	108.0	14	75	753	0.33	0.40
0.410	1.0077	**(002)** **(200)**	33(2) 64(2)	27	7518	106.6	56	46	937	0.37	0.40
0.064	1.0079	**(002)** **(200)**	29(2) 56(2)	13	7579	106.0	72	84	1650	0.38	0.48

Conclusion

Different microstructures of barium titanate ceramics are repercussive onto their electrical properties. Smaller average grain size enable enlarged both dielectric constant and grain boundary resistivity. It is shown that the initial particle size of the powder have a limiting influence on the grain size in the sintering process. It is also shown that electrical characteristics of barium titanate ceramics primary depend on the average grain size of sintered samples. All investigated properties, including dielectric constant and grain boundaries resistivity, increase with decreasing of average grain size. It can be emphasized that electrical characteristics of sintered ceramics are very sensitive to grain size and to shape of grain boundaries. So, fine-particles BT powders are desirable for higher grain boundary resistivity.

Impedance spectroscopy shows that the electrical behavior of grain boundaries depends on ceramics microstructure and consequently on starting powders' average particle size.

The samples presented here are very resistive. This indicates their high quality as insulating materials.