

The Correlation between Particle Size and Sintering Temperature using Barium Titanate (BaTiO₃) as an Example



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Synopsis:

The influence of the primary particle size on the sintering behavior of ceramic green bodies was systematically tested on several series of samples. Barium titanate (BaTiO₃) served as a model system; due to its good ferroelectric, dielectric and pyroelectric properties, its application in electronics and sensor technology is quite versatile.

It was demonstrated that ready-for-use mixtures of barium titanate show ever lower sintering temperatures as the mean particle size (d₅₀) decreases.

Introduction:

Barium titanate crystallizes in the temperature range from -100°C to 150°C in four different modifications (Fig. 1). The phase change temperatures and their enthalpies can be determined with the help of Differential Scanning Calorimetry (DSC) (Fig. 2).

Crystal Structure	Temperature Range (°C)	Parameters
ideal cubic	1200 - 1500	a = b = c = 399.6 pm
tetragonal	150 - 1200	a = b = 399.8 pm, c = 402 pm
orthorhombic	120 - 150	a = 401 pm, b = 400.8 pm, c = 397 pm
rhombic	120 - 150	a = b = c = 399.5 pm, α = β = γ = 90°, α ₁ β ₁ γ ₁ = 90°, <120°

Source: Silvio Gablitz, Diss. Uni Halle, 2001

Fig. 1: The modifications of barium titanate

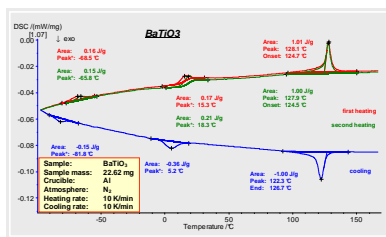


Fig. 2: DSC results for the characterization of phase transitions of barium titanate

The cubic modification, stable at temperatures over 125°C, exhibits Perovskite structure (ABX₃). The tetragonal modification existing at room temperature can be described as a distortion of this cubic structure, in which the central titanium atom within the oxygen octahedron is shifted from the center toward an octahedral corner.



As a result of this distortion, a polar axis is created which in turn makes polarization possible, thereby fulfilling the condition for the formation of ferroelectric properties. The phase change temperature can be varied by doping with foreign cations.

Results:

In order to optimize properties, barium titanate powders are often mixed with additives that, among other effects, also specifically influence the phase changes of pure barium titanate. Figure 3 shows a mixture for which the temperature of the phase change, tetragonal to cubic, was shifted to about 140°C and the change was no longer detected as a peak, but rather only as a change in the specific heat of the sample.

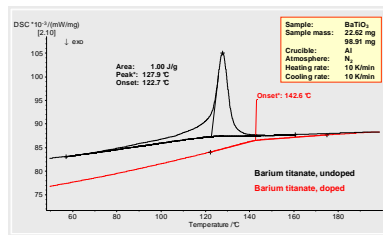


Fig. 3: Comparison of the phase change temperature of two barium titanate samples (tetragonal to cubic)

To test the sintering behavior, the calcined powder samples were fine-milled in an aqueous suspension with a NETZSCH Laboratory Agitator Bead Mill (Type LS1) in circular operation for up to 180 min.

The particles (agglomerate), originally up to 1 mm in size, were thereby ground to mean d₅₀ values of between 3 μm and 100 nm.

Measurement results:
 Diameter on Cumulative % : (100.00%) - 98.8776(μm)
 : (99.00%) - 97.2897(μm)
 : (10.00%) - 10(μm)

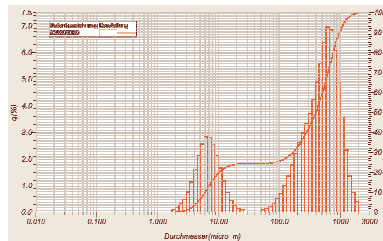


Fig. 4: Results of the determination of particle size for the calcined barium titanate

Figures 4 and 5 depict the particle size distribution of both the calcined original material and the ground sample which was attained. To stabilize the fine particles against reagglomeration, it was necessary to add a dispersing agent.

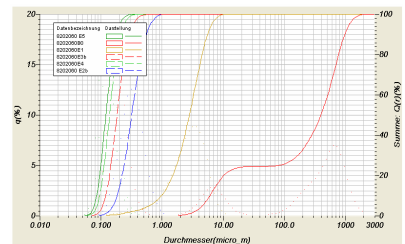


Fig. 5: Results of the fine grinding of barium titanate

In order to test the sintering behavior, the powders were dried for 12 h at 120°C in a drying chamber and thereafter compressed with a molding press (5 kN) into cylindrical sample shapes (l = 3-4 mm, Ø = 5 mm). The sintering behavior of these was then tested with a push rod dilatometer (NETZSCH DIL 402 C). The results from the samples without a dispersing agent are depicted in Figure 6. Figure 7 shows that, by fine-milling the barium titanate samples from 10 μm to 0.13 μm, it was possible to reduce the sintering temperature by 100 K to 1100°C.

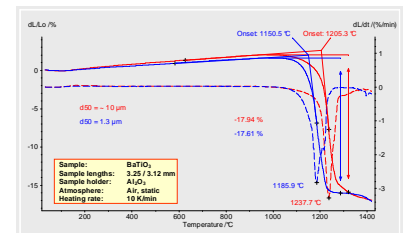


Fig. 6: The sintering results of two barium titanate samples

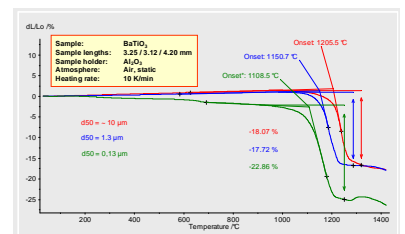


Fig. 7: The sintering results of samples up to 0.13 μm

Energy-reducing developments in the ceramics field are particularly interesting in the current context of heated discussions regarding CO₂ problems.