PREPARATION OF BARIUM TITANATE AEROGELS BY SUPERCRITICAL DRYING WITH CO_2 AND PROPANE

Z. Novak, Ž. Knez*, I. Ban and M. Drofenik

Faculty for Chemistry and Chemical Engineering, University of Maribor, Smetanova 17, SI-2000 Maribor, Slovenia
E-mail: zeljko.knez@uni-mb.si; Fax: +386 2 2516 750

Barium titanate powders from sol-gel prepared gels were derived by drying the gels in supercritical CO_2 and near critical propane at 40 °C. Results show that $BaTiO_3$ (BT) powders prepared by drying using liquid propane do not agglomerate. Besides, coarsening and densification of compacts prepared from these powders are retarded. Sintered samples prepared from these powders lead to a homogeneous fine-grain microstructure.

INTRODUCTION

The investigation of advanced ceramic materials is related to the study of ceramic powders with small grains, in particular the study of nano-sized powders which are used during the preparation of electronic ceramics. Different methods of synthesis for fine ceramic powders are well known, for example: co-precipitation, spray drying, spray freezing, hydrothermal synthesis and the sol–gel procedure [1-3]. Among these processes the sol-gel procedure is promising since enables the control of the homogeneity and reactivity of the ceramic powders to a large extent. Sol–gel techniques are increasingly used for the production of high technology ceramics, due to superior electronic properties, mechanical stability and chemical purity. One of the important steps during powder synthesis using the sol-gel procedure is the drying of the gels. Many important powder properties, for example: homogeneity, the size of the agglomerates and the extent of agglomeration are developed during this important step of powder synthesis. The drying of gels is certainly a key process when it comes to the final properties of the powder, this is particularly true when controlling the powder agglomeration. Essential electronic and mechanical properties, reflected in the microstructure, are determined to a large extent by the drying stage of the gels.
Gels are usually dried for long times in air at elevated temperatures. In our recent work the supercritical CO_2 [4] was used to dry and prepare submicron BT powders. However, the CO_2 reacts partially with BaO forming $BaCO_3$ what might change the powder properties. In the course of this work propane was used instead of CO_2.
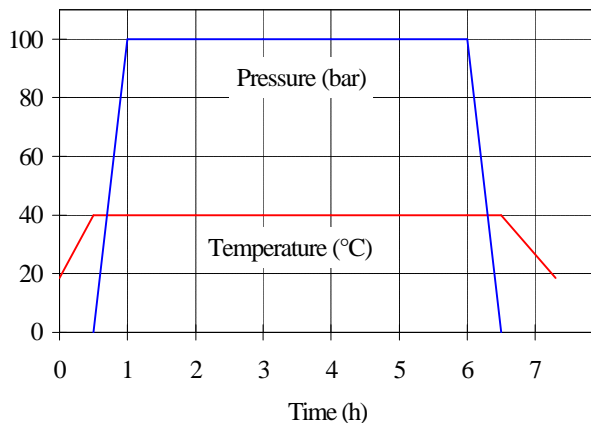
EXPERIMENTAL

Different BaTiO$_3$ powders were prepared by two different drying methods for sol-gel derived BaTiO$_3$ gels. Besides supercritical drying of gels with CO$_2$, near critical drying with liquid propane was also applied to compare the properties of both BaTiO$_3$ powders (Figure 1).
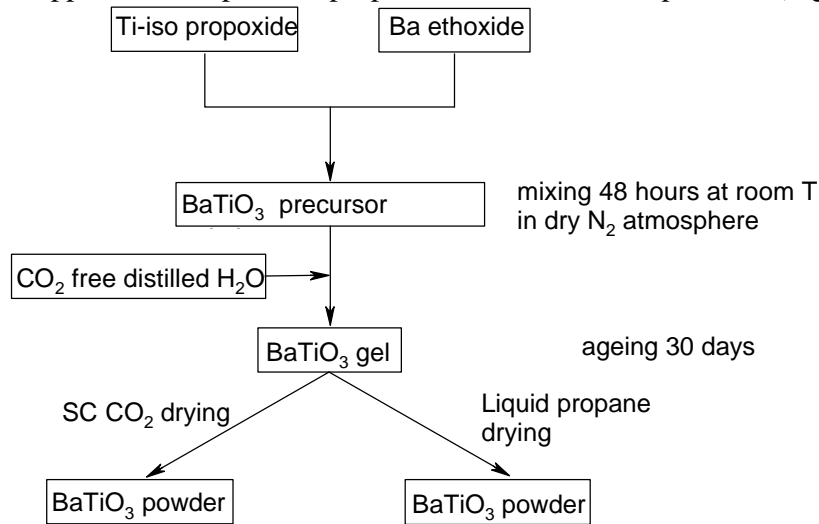
Figure 1: Scheme for experimental procedure for synthesis of barium titanate.

Sol-gel synthesis. For the preparation of BaTiO$_3$ gels, titanium(IV) isopropoxide, Ti(OCH$_2$(CH)$_3$)$_4$, (Aldrich, purity 99.99%) and barium ethoxide, Ba(OCH$_2$CH$_3$)$_2$, (Aldrich, purity 99,99%, 10 wt % solution in pure ethanol) were used in equimolar amounts (Ba:Ti = 1:1). The synthesis of Ba-Ti precursor alkoxide mixtures was performed in a dry nitrogen atmosphere. After adding CO$_2$-free distilled water the hydrolized solutions were aged for 30 days at room temperature.

Figure 2: Experimental conditions for supercritical CO$_2$ and liquid propane drying

Propane drying. After gelation was terminated, the gels were dried in supercritical CO$_2$ and liquid propane at 40°C and 100 bar (Figure 2). The procedure and conditions for the second drying method with liquid propane were the same as for supercritical CO$_2$ drying, well described in our previous papers [4,5], with the exception that at this condition propane is in liquid state.

Characterization. The powders were inspected with transmission electron microscopy (TEM). The specific surface was measured using BET method and x-ray powder diffraction patterns were taken. The crystallite size of BaTiO$_3$ was estimated using the Scheerer equation, from the (200)

diffraction peak. In addition, the shrinkage of the samples prepared from both powders was determined and the microstructure of polished and etched samples was investigated.

RESULTS AND DISCUSSION

Fig. 3 shows TEM images of $BaTiO_3$ powders dried in liquid propane and the same powder calcined at 1100 ^{o}C. It can be seen that the synthesised powder (Fig. 3a) composes of crystallites whose size can be measured in nanometers. Besides, this powder is not agglomerated. On the other hand, the calcined powders show larger crystallites indicating coarsening. However, that powder is also not agglomerated (Fig. 3b).

a.)   b.)
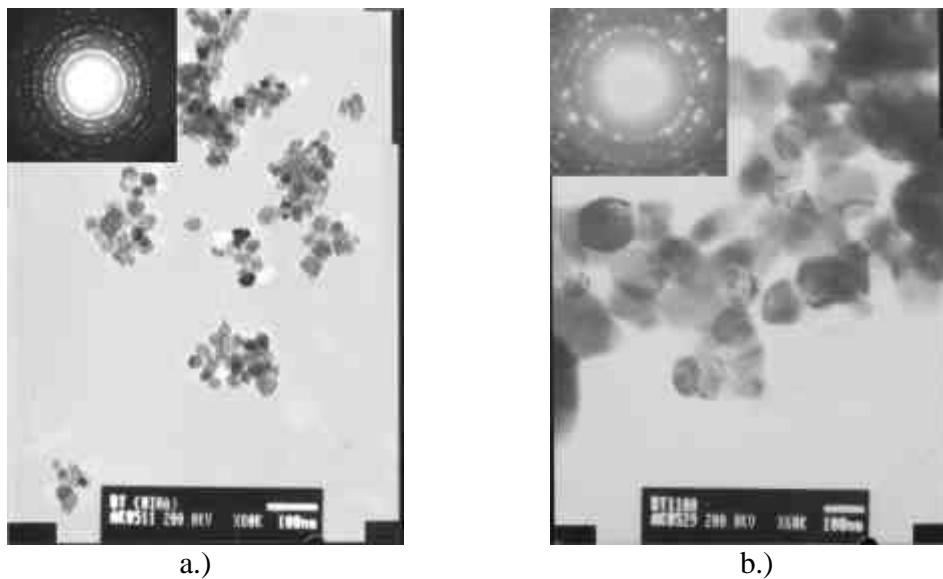
Figure 3: TEM images of $BaTiO_3$ powder: a) after drying with liquid propane and b) after calcination at 1100 ^{o}C for three hour on air.

The x-ray powder diffraction patterns of dried powders and of calcined powders are shown on Fig. 4. The x-ray diffraction of powders show diffraction peaks of $BaTiO_3$ and $BaCO_3$.
The $BaTiO_3$ crystallite size was determined by the Scherrer relation $d_x = 0.94\ \lambda/\ \beta\ \cos\theta$ where λ (1.5406 Å) is the characteristic wave length, β is the true half peak width and θ half the diffraction angle of the centroid of the peak (in degrees).

Table 1: Specific surface area (S) and the average grain size d_x and d_s obtained from the diffraction data and from the specific surface measurements respectively.

| Sample BT	S(m^2/g)	d_x(nm)	d_s(nm)
dried powder	95,7	20,4	10,0
calcined powder (1100°C)	2,71	/*	367,7 (0,367μm)

*the cristallite size is too large.

The size of the crystallites obtained from the Scheerer equation is larger than that estimated from the specific surface area (S) for both powders. The differences in the average size between d_x and that obtained from the specific surface d_s ($d_s = 6V_m/S$, where V_m is mol volume of $BaTiO_3$ and (S) is the measured specific surface) appears when the shapes of the crystallites can not be taken as perfect spheres.
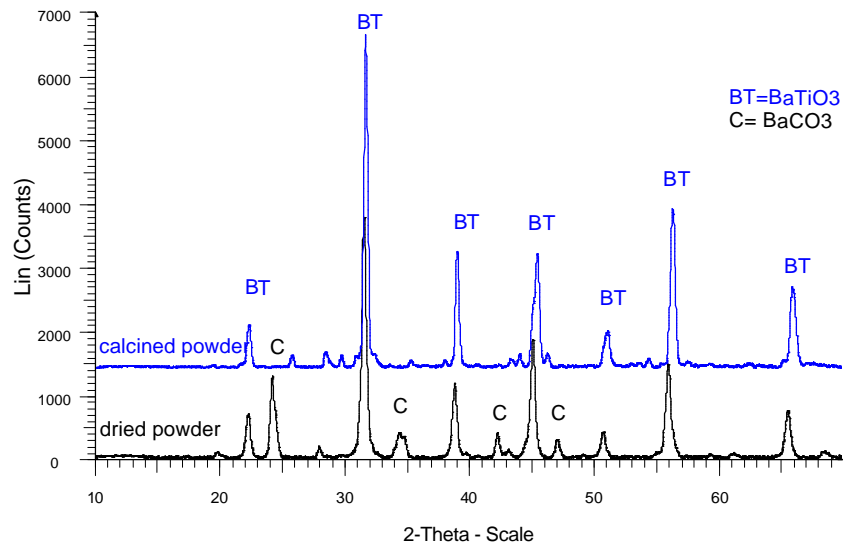

Figure 4: X-ray diffraction patterns of synthesised powders and of calcined powders at 1100 °C.

The powder prepared by drying in propane has low tap density, approximately 0,97 g/cm^3. The density of compacts 55% was obtained when the powder was pressed with a pressure of about 10^8 Pa.

On Fig. 5 the shrinkage and corresponding shrinkage rate spectra of samples during sintering is shown. Samples show only one pronounced maximum in the shrinkage rate at 1200°C indicating that grains behave very uniform. The final density of the samples after sintering in air, with respect to the theoretical density, was 94%. The sintering temperature profile was not optimised.
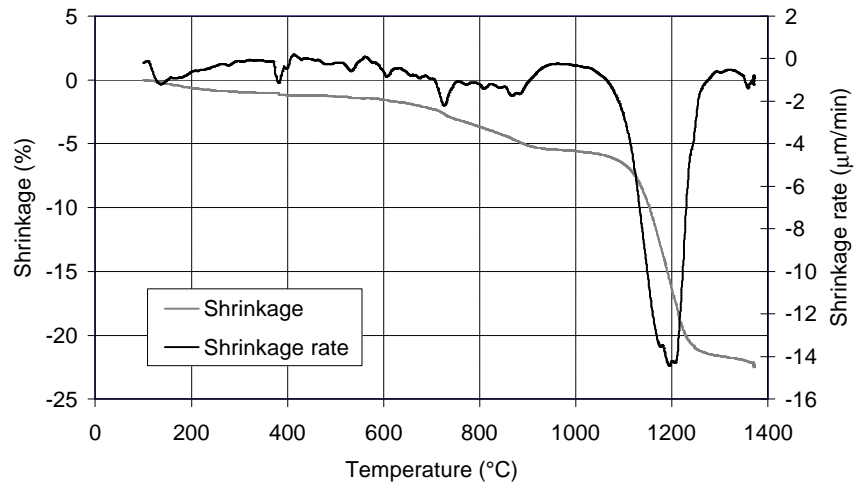
Figure 5: The shrinkage spectra of BaTiO₃ powder dried by liquid propane.

The microstructure of samples after sintering is shown in the Fig. 6. The samples show a relatively dense microstructure with an average grain size of about 4 μm.
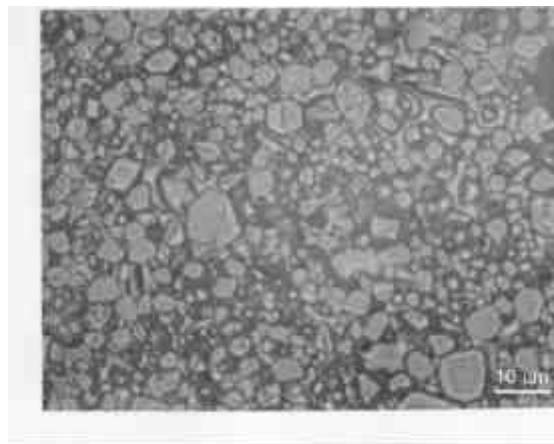

Figure 6: Microstructure of sample sintered at 1350 $^{\circ}$C for 1 hour in air.

For BaTiO$_3$, discontinuous grain growth is the main process of microstructure development. In this process, some small fractions of the grains in a matrix of similar grains outgrow on account of neighbouring grains. For this discontinuous grain growth to occur, firstly the nucleus grains have to be formed. They grow much faster in comparison to other grains in the matrix [6]. The final microstructure depends to a large extent on the number of these nucleus grains.

When the powder is prepared by drying of BT in the liquid propane, the propane dissolves and washes away the organic disintegration products and inhibits the agglomeration of powder particles. The absence of agglomerates decreases the total number of grains with the overestimated grain size which otherwise strongly promotes the anomalous grain growth.

On the basis of retardation of coarsening and densification which starts after 1000 $^{\circ}$C, although the sintered powder consists of nano particles with an average grain size of 10nm, one may conclude that liquid propane passivates the nano-particle surface and retards the coarsening and the densification up to about 1000 $^{\circ}$C. Such a passivity might occur when the nanoparticle surface is covered with a nano-layer of propane adsorbed during treating the powder in liquid propane. Such a thin layer of hydrocarbons may passivate the surface as long as it is adsorbed to the particles surface. These layers can also prevent agglomeration because of their non-polar character.

The TG analyses in combination with mass spectroscopy (Fig. 7) show that the intensive release of CO_2, which is most probably a result of the disintegration of $BaCO_3$ and propane oxidation, terminates at about 1000 $^{\circ}$C. This is the temperature where the intensive shrinkage of compact starts. Thus, above 1000 $^{\circ}$C the surface of BT nano-particles becomes free of the most of disintegration products and the surface diffusion can take place leading to intensive shrinkage and/or densification.
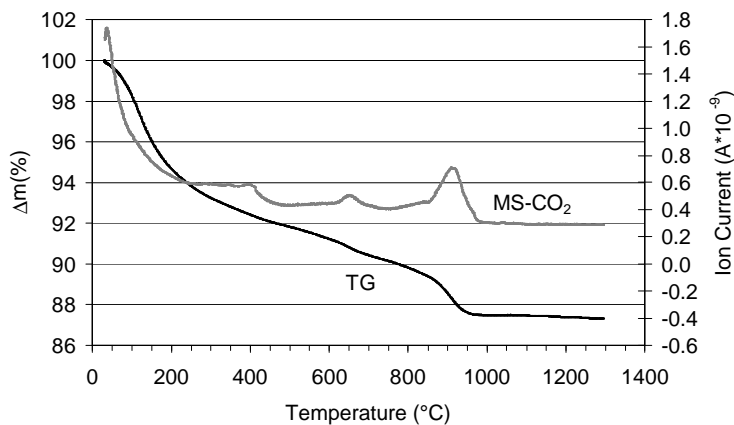
Figure 7: DTA/TG analysis of propane dried powders with mass spectra analysis.

CONCLUSIONS

No notable anomalous grain growth was observed during sintering of $BaTiO_3$ compacts prepared from powders treated with liquid propane. Besides, the retardation of coarsening and densification of powder and/or compacts was observed. Such retardation was most probably the result of a nanoparticle surface passivity due to the formation of a thin layer of adsorbed propane. When the layer was removed during heating the samples on air, an intensive densification of compacts during sintering could be observed.

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