Hydrothermal Synthesis of Nanocrystalline Perovskite Powder Systems

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Nanocrystalline perovskite phase powders like PZT or $BaTiO_3$ were synthesized using colloidal wet chemical processing and low temperature crystallisation steps. For production of PZT powder an aqueous precursor system was synthesized. The precursor system was precipitated by using a 4 molare potassium hydroxide solution. The resulting mixture of Pb-, Zr- and Ti-hydroxide was treated in an autoclave system at temperatures up to 250 °C to promote the crystallization of the perovskite phase of PZT. $BaTiO_3$ powders were synthesis using a solution of $BaCl_2$ and $TiCl_4$ which becomes heated at temperatures of about 130 °C. The powders were characterized using x-ray diffraction, TEM and specific surface measurement by BET method. Particle size distribution was measured with laser light scattering method. Influence of organic additives onto crystallization behavior and agglomeration of the PZT powders was monitored.

Keywords: perovskite powders; lead zirconate titanate; barium titanate; hydrothermal synthesis

INTRODUCTION

Perovskite phase powders like lead zirconate titanate or barium titanate are of widely interest because of their ferroelectric abilities. Normaly microscaled powders synthesized by solid state reaction of the pure oxides were used as precursor materials. Green bodies were formed by slurry technology and then sintered at high temperatures (for PZT about 1200 °C) to dense bulk materials.

After poling the material will be used as active material for ferroelectric or piezoelectric components like sensors and actuators.

Additional PZT or $BaTiO_3$ powders were used in tape casting techniques to produce thick films (up to a few hundred micrometers) wich will be used in the same manner as the bulk material.

Using bulk materials with a thickness in the mm range in electronic components causes a strong mismatch between the voltage used in the electronic parts (about 5 V) and the electric field which is necessary to switch the ferroelectric material (about 1 kV / mm). Therefore an additional electric connection (e.g. transformation of the voltage) has to be build up between the electronic parts and the bulk material which enlarges the total volume of the component.

Now the potential use of nanocrystalline and submicron to nanometer scaled powders promises the advantage of the accessiblity of micrometer thick materials with very smooth surfaces wich can be used in electronic components without an additional eletric connection. Therefore future electronic components will be much more smaller, cheaper than present ones and the field of applications will be strongly broaden.

The availability of a nanoscaled powder requests a synthesis wich leads to a aggregation free well dispersible powder. In contradiction to these demand the common synthesis of perovskite phase powders is the solid state reaction of metal oxides which leads to high aggregated particles with size distribution in the micrometer range and higher. But a powerful tool to produce submicrometer or nanometer sized and aggregation free particles will be the hydrothermal synthesis. These process promotes the crystallisation at temperatures from 70 °C - 200 °C [1], to 150 °C - 350 °C [2] in an autoclave system. Different mostly inhomogenous precursor systems like mixtures of titanium oxide chloride ($TiOCl_2$) [2], titanium chloride ($TiCl_4$) [1,3,4,5], titanium butylate ($Ti(OC_4H_9)_4$) [6] or titanium hydroxide ($Ti(OH)_4$) [7] with zirconium oxide chloride ($ZrOCl_2$) [1,2,3,4,5,6] and lead oxide (PbO) [2,3], lead nitrate

$(Pb(NO_3)_2)$ [1, 4, 5] or lead acetate $(Pb(CH_3COO)_2)$ [6, 7] were described. Ammonia hydroxide and potassium hydroxide solutions with concentrations from 1 mol/l [6] to 10 mol/l [1] are in common use to precipitate hydroxides and to promote the crystallization of the perovskite phase during the hydrothermal reaction.

The reported particle size is in the range of 0,1 μm to 5 μm and sometimes no pure perovskite phase but additonal metal oxide phases are obtained.

The use of surface active substances to reduce the agglomeration and aggregation of the particles wasn't reported although the low processing temperatures of these process allows the use of organic surface active substances. These additives will minimize the free surface energy of the as precipitated particles and prevent agglomeration and aggregation during the following step of crystallization. Therefore agglomerate and aggregate free submicron and nanometer sized particles must be available.

EXPERIMENTAL

Synthesis of PZT powders

A homogeneous aqueous precursor system was synthesized be using a method described by G. Rinn[8]. Therefore Ti-isopropanole and Zr-n-propanole were dissolved in waterfree ethanole and then hydrolysed by addition of diluted nitric acid. After this a white sol was achieved from which the alcohols were removed by evaporation. The same amount of water was added to get a clear transparant aqueous zirconium hydroxide / titanium hydroxide sol. Now a stoichiometric solution of lead nitrate was added to achieve an aqueous PZT precursor system.

The precursor system was precipitated with a 4 molare potassium hydroxide solution to form a complex lead zirconium titantium hydroxide. The resulting

white supension was filled in autoclave system and heated at different tempe-
ratures from 150 °C to 250 °C for 1 to 20 hours. Organic substances were ad-
ded for surface modification of the powders during crystallization step. After
finishing the reaction the powders were washed and dried. Crystallization be-
havior of the powders depending on synthesis conditions like reaction tempe-
rature, reaction time and kind of organic modifier were monitored.

Synthesis of BaTiO_3 powders

The synthesis of $BaTiO_2$ powders was similiar to a procedure described by
Klee [9]. It starts with an aqueous solution of $BaCl_2$ to which $TiCl_4$ is added
while stirring. After heating up the mixture to 120 °C to 130 °C for 16 h the
hydrochloric acid is removed by destillation and a sol of $BaTiO_3$ particles in
water is obtained. The powder was isolated, washed and dried.

Both powders were characterized according to their crystalline phase, primary
particle size, specific surface and dispersibility. X-ray diffraction with a Sie-
mens D 500 x-ray diffractometer with Cu-Kα radiation was used to characte-
rize the crystalline phase of the powders. Crystallite size of the powders was
calculated by Scherrer function.

High resolution scanning electron microscopie with a JEOL (JSM 6400 F) was
used to characterize particle morphologie. Laser light scattering method with
an Ultrafine Particle Analyser (UPA) from Grimm was used for determination
of the particle size distribution and specific surface was measured by the BET
method with a micromeretics ASAP 2400 system. Powder density was
measured with a gas pycnometer.

RESULTS AND DISCUSSION

PZT powder

To investigate the influence of the reaction conditions onto the powder abilities different temperatures from 150 °C to 250 °C were adjusted for the hydrothermal crystallization. Afterwards different reaction times at constant temperature were chosen to find the best performamce. Then surface active substances were improved to reduce the agglomeration of the powders.

FIGURE 1 shows the x-ray diffraction pattern of PZT powders wich were hydrothermal crystallized at temperatures of 150 °C to 250 °C and in the figure capture the crystallite size of the powders is writen down. Even at 150 °C the crystallization of the perovskite phase occurs and with raising temperature the intensity of the reflections increases which indicates an increasing amount of the perovskite phase. In contrary no increase in crystallite size was observerd which is always in the range of 20 nm.

FIGURE 2 and FIGURE 3 are showing the x-ray diffraction pattern of powders crystallized with reaction times of 1 h to 20 h at 150 °C and 250 °C respectivly. At 150 °C were is a strong influence of the reaction time onto the intensity of the reflections but not onto the crystallite size which is always in the range of 20 nm. At 250 °C the influence of the temperature onto the reflection intensity isn't as strong as at 150 °C and additional there is also no markable influence onto the crystallite size. According to the results from these investigations a temperature of 250 °C and a reaction time of 5 h were chosen as standard conditions for powder synthesis. These conditions were used to perform investigations about the influence of the organic additives onto the powder abilities as crystallinity and agglomeration behavior. Therefore complex forming agents as citric acid and acetyle acetone and surface active substances as emulsifier (Tween 80) and ethylene glycole were tested.
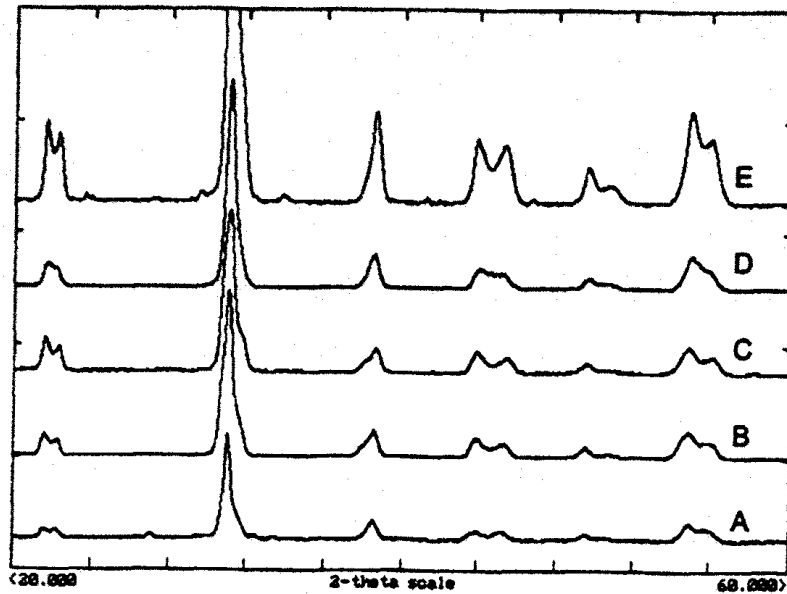
FIGURE 1   X-ray diffraction pattern of PZT powders, hydrothermaly synthesized at different temperatures with a reaction time of 20 h A) 150 °C (20 nm) B) 175 °C (23 nm) C) 200 °C (21 nm) D) 225 °C (17 nm) E) 250 °C (20 nm)
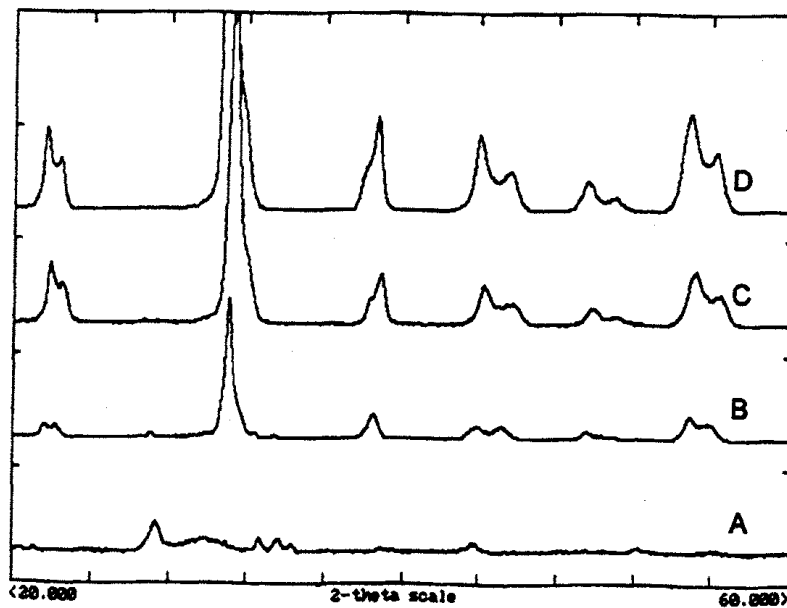

FIGURE 2   X-ray diffraction pattern of PZT powders, hydrothermaly synthesized with different reaction times at 150 °C A) 1 h (no perovskite) B) 5 h (20 nm) C) 10 h (18 nm) D) 20 h (19 nm)
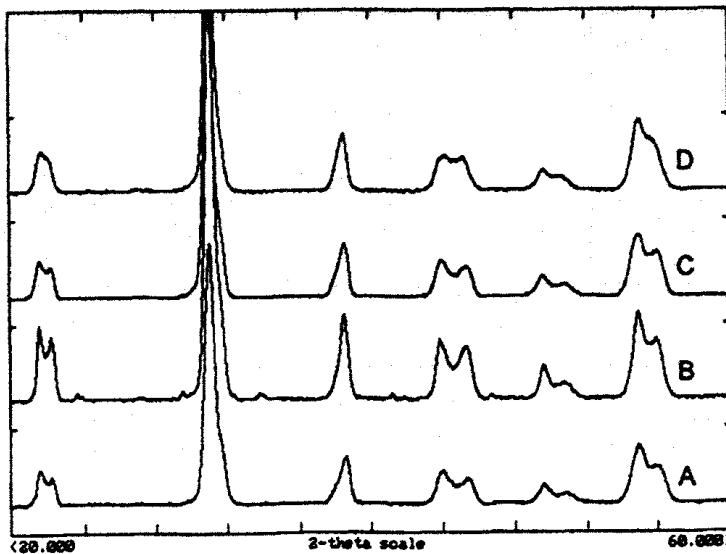
FIGURE 3   X-ray diffraction pattern of PZT powders, hydrothermaly synthesized with different reaction times at 250 °C A) 1 h (16 nm) B) 5 h (20 nm) C) 10 h (24 nm) D) 20 h (18 nm)

In FIGURE 4 the x-ray diffraction pattern of powders synthesized with the mentioned organic additives are shown. Using complex forming agent as citric acid (c) and acetyle acetone (d) no crystallisation of the desired perovskite phase was observed. With ethylene glycole (e) and the emulsifier (b) a perovskite phase PZT was obtained. It is noteworthy that the x-ray diffraction pattern of the powder modified with emulsifier is very similiar to the one without any additive. So the use of the emulsifier promises the lowest influence onto the crystallisation behavior of the powder. To monitore the influence of the emulsifier onto the particle size distribution was measured with dynamic light back scattering method (Ultrafine Particle Size Analyser - UPA, from Grimm). FIGURE 5 shows the particle size distributions of PZT powders dispersed in water (volume and number distribution with d_{10}-, d_{50}- and d_{90}-values for a powder without additive (A), without additive electro statical stabilized (B), with emulsifier (C) and with emulsifier electro statical stabilized (D).
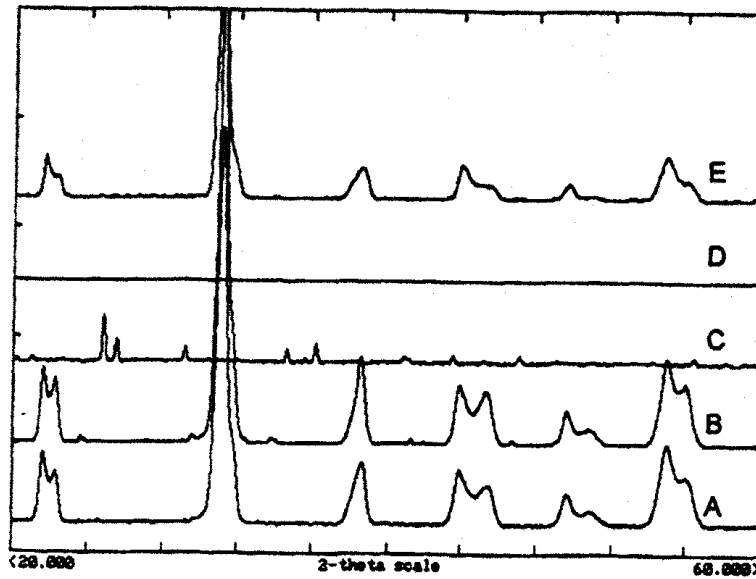
FIGURE 4 X-ray diffraction pattern of PZT powders, hydrothermaly synthesized with different organic additives at 250 °C for 5 h A) no additive (22 nm) B) Emulsifier (20 nm) C) citric acid (no PZT) D) acetyle acetone (amorphous) E) ethylene glycole (19 nm)
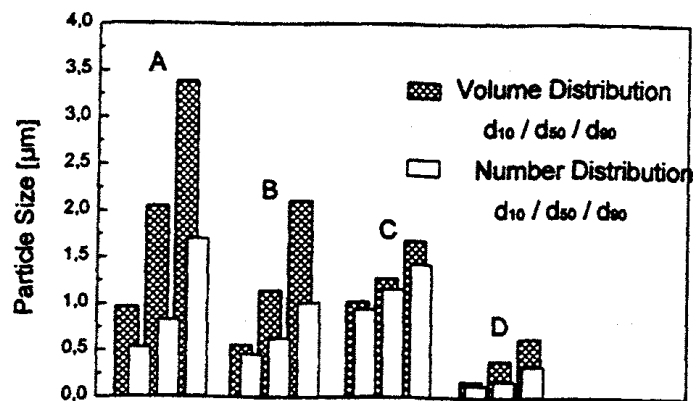

FIGURE 5 Particle size distribution of PZT powders (volume and number distribution with d_{10}-, d_{50}- and d_{90}- values from left to the right A) without additive, B) without additive electro statical stabilized C) with emulsifier D) with emulsifier electro statical stabilized

Using the emulsifier with an electro statical stabilization the particle size distribution could be lowered from $d_{90}(V) = 3,4$ µm to $d_{90}(V) = 0,6$ µm compared with the powder without modification.

FIGURE 6 shows the SEM picture of a powder modified with the emulsifier. Cubic primary particles with a size distribution in the range of 100 nm up to 600 nm are visible. This observation corresponds to the measured particle size distribution of $d_{90}(V) = 0,6$ µm. Some agglomerates with a size up to 1 µm also present.
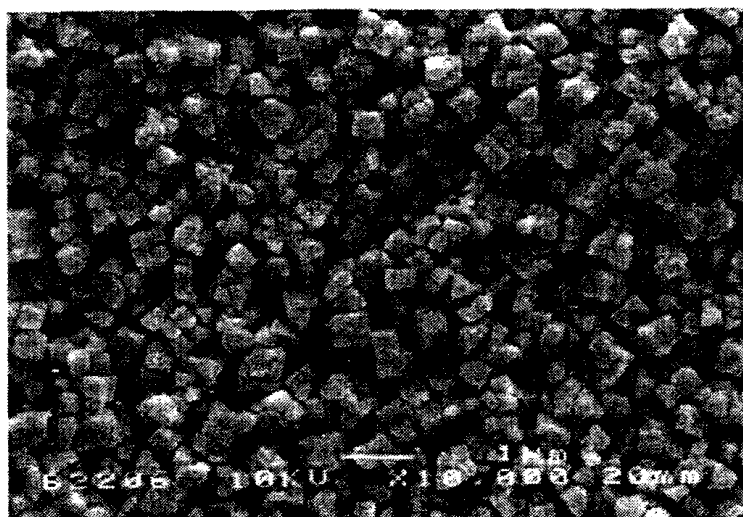

FIGURE 6   SEM picture of hydrothermaly synthesized PZT powder (5 h at 250 °C - density 7,8 g/cm^3 = 97 % of th., specific surface area 8 m^2/g)

The powder has a density of 7,8 g/cm^3 (97 % of th.) and a specific surface area of 8 m^2/g was measured by BET. This value corresponds with an average particle size of about 100 nm.

Future work will be done in the field of surface modification. Therefore other kinds of emulsifiers will be tested as well as different amounts of the agent depending on the surface area of the powders.

<u>BaTiO$_3$ powder</u>

The synthesis of BaTiO$_3$ powders was only performed in one way without any changes in reaction conditions. Also organic additivs for surface modification are not yet used.
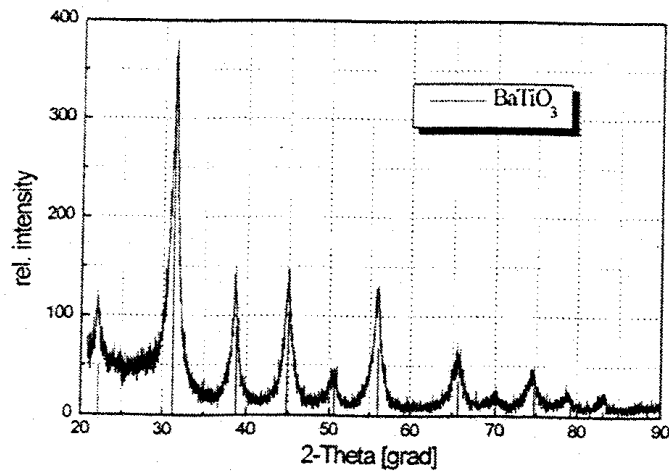

FIGURE 7   X-ray diffraction pattern of BaTiO$_3$ powder, JCPDS card no. 31-174 underlayed, crystallite size 15 nm
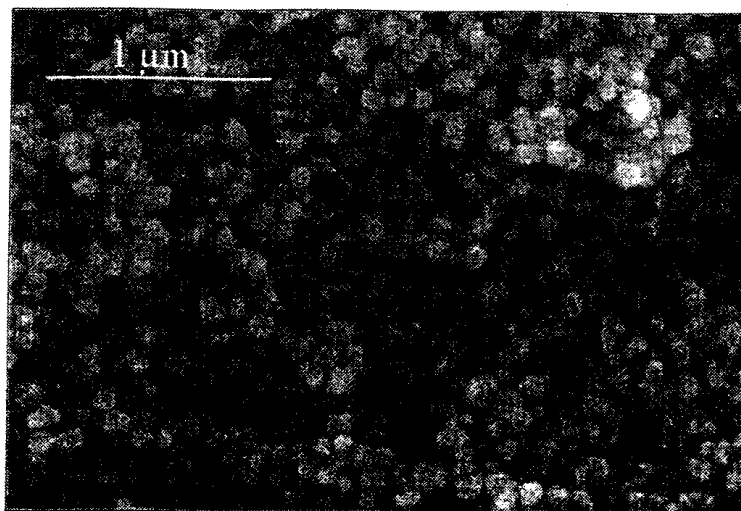

FIGURE 8   SEM picture of BaTiO$_3$ powder, density 5,5 g/cm^3 (91 % of th.), specific surface area 18 m^2/g

FIGURE 7 shows the x-ray diffraction pattern of the $BaTiO_3$ powder with the underlayed JCPDS card no. 31-174. The Powder has the pure cubic phase of Ba TiO_3 with a calculated crystallite size of about 15 nm

FIGURE 8 shows the SEM picture of the $BaTiO_3$ powder. The particles have spheric shape and a primary particle size is in the range of 45 nm to 60 nm with a narrow distribution. Only a few agglomerates are visible.

Powder density is about 5,5 g/cm^3 (91 % of th.) and a specific surface area of 18 m^2/g was measured by BET. This value corresponds with average particle size of about 60 nm.

Further investigations will be done in future to monitoring the influence of process parameters onto powder properties and additional the use of surface active substances will be improved in the same manner as in the case of PZT.

SUMMARY

Wet chemical processing was sucessfully used for synthesis of finescaled nanocrystalline perovskite phase powders. In the case of PZT the hydrothermal crystallisation leads to a primary particle size of 100 nm to 600 nm. The influence of hydrothermal reaction conditions onto the crystallisation behavior of the powders were monitored and the best values were found to be 250 °C for 5 h. Surface active substances were tested to reduce agglomerate size. Using emulsifier agglomerate size could be reduced to a the range below 1 µm which is in the dimension of the primary particle size.

Weakly agglomerated $BaTiO_3$ powders could be synthesized with a primary particle size in the range of 45 µm to 60 µm.

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