

Preparation of Submicrometer Ferroelectric Particles by Wet-Chemical Methods

S. Schlag,[†] H.-F. Eicke,^{*,†} D. Mathys,[‡] and R. Guggenheim[‡]

Institute of Physical Chemistry, Department of Chemistry, and SEM-Laboratory, University of Basel, Switzerland

Received February 25, 1994. In Final Form: June 9, 1994[®]

Submicrometer particles of triglycine sulfate and BaTiO₃ have been prepared using precipitation from reverse microemulsion nanodroplets and hydrolysis of organometallic compounds. Size, size distribution, and morphology of the particles were determined by transmission electron microscopy, conventional scanning electron microscopy, and field emission scanning electron microscopy. Structural analysis was carried out by X-ray powder scattering.

Introduction

The synthesis of submicrometer ferroelectric particles attracts interest for several reasons. In the case of ferroelectric oxides, powders consisting of ultrasmall particles can serve as excellent starting material for the production of ceramic materials. Furthermore, the smaller the ferroelectric particles are, the easier they can be dispersed homogeneously in organic solvents, polymer matrices, or water and thereby transport their anisotropic properties in the respective media. Another interesting question concerning submicrometer ferroelectric particles is the critical size below which ferroelectricity disappears. This question, which is a matter of discussion, is of growing importance for the fundamental understanding of the properties of ferroelectric thin films, used in various applications in microelectronic devices.

In the case of BaTiO₃, many techniques are reported in the literature for the synthesis of small particles. First is the ball-milling technique, where particles of any size can be produced. The disadvantage of this method is that it takes a long time to produce submicrometer particles, and mechanical stresses may cause distortion in the surface region of the particles.¹⁻³

Through sputtering methods⁴ and electrophoretic deposition,⁵ thin films of BaTiO₃ were produced with grain sizes down to 20 nm.

Wet-chemical synthesis methods include the production of small BaTiO₃ particles by precipitation of the mixed oxalate, followed by calcination. Particle size is limited because heat treatment is necessary during calcination. A minimum grain size of 50 nm was reported from Pfaff et al.⁶ in 1992. A review on further chemical methods such as the sol-gel process, citrate process, and the alkoxide route is given by Phule et al.⁷

Recently, the few nanometer-size water droplets of reverse microemulsion were used as "nanoreactors" for chemical synthesis. They provide the chance for production of nanosize particles with a narrow size distribution.^{8,9,15} In analogy to the preparation of superconducting

Table 1. Compositions of the Microemulsions Used

sample	TGS soln [g]	oil (decane) [g]	surfactant (Genapol OX30) [g]
TGS 1	5	70	10
TGS 2	6	70	10
TGS 3	7	70	10

oxides,¹⁰ we attempted to carry out the precipitation of the mixed Ba, Ti oxalate in a microemulsion. Because this method yielded no pure BaTiO₃, we chose a second method: the hydrolysis of alkoxides. With this method, a very pure, stoichiometric material can be produced.^{11,13}

As far as we know, in the case of triglycine sulfate (TGS), no efforts have been made on the synthesis of small particles.

Because TGS is soluble in water, the known methods of synthesis in microemulsions are not possible. Our idea is to use the microemulsion for homogeneous distribution of TGS in small portions and to force precipitation of nanosize material by evaporation of the water droplets.

Materials and Methods

TGS-Synthesis. All the chemicals used (decane practical (Fluka, >96%), nonionic surfactant Genapol OX 30 (Hoechst)) were of commercial grade and used without further purification. Deionized distilled water was used in all the chemical procedures. Macrocrystalline TGS was precipitated from supersaturated solution and washed as described by Nitsche et al.¹² The glycine (puriss. p.a., Fluka) and the sulfuric acid (puriss. p.a. 95-97%, Fluka) were used without further purification. A 0.5 M TGS solution was prepared and dissolved in the oil/surfactant mixture to form stable nanodroplets in the microemulsion (ME) system whose composition is given in Table 1. Because the size of the droplets is given by the volume fraction of oil and water, the size of the droplets increases with increasing water content (Figure 1).

The procedure of precipitation is schematically shown in Figure 1. Evaporation was done in the temperature region where the ME (i.e. the nanodroplet structure) is stable. The ME was heated for this purpose in a water bath with stirring. After equilibration at that temperature, the reaction vessel was connected to the vacuum pump and evaporated until precipitation occurred. The mixture was then centrifuged and freeze-dried. Since most of the surfactant remained on the powder, determination of particle

[†] Institute of Physical Chemistry.

[‡] SEM-Laboratory.

[®] Abstract published in *Advance ACS Abstracts*, August 15, 1994.

(1) Anliker, M.; Brugger, H. R.; Känzig, W. *Helv. Phys. Acta* **1954**, *27*, 99.

(2) Müller, J.-U.; Bärner, K. *Ferroelectrics* **1990**, *108*, 83.

(3) Müller, J. U.; Abendroth, J.; Bärner, K. *Int. Conf. Conduct. Breakdown Dielectr. Liq.* **1990**, *10*, 464.

(4) Horikawa, T. *Jpn. J. Appl. Phys.* **1993**, *32*, 4126.

(5) Okamura S.; Tsukamoto, T.; Koura, N. *Jpn. J. Appl. Phys.* **1993**, *32*, 4182.

(6) Pfaff, G. *J. Mater. Sci.* **1992**, *27*, 1222.

(7) Phule, P. P.; Risbud, S. H. *J. Mater. Sci.* **1990**, *25*, 1169.

(8) Osseo-Asare, K.; Arrigada, F. J. *Ceram. Trans.* **1990**, *12*, 3.

(9) Barnickel, P.; Wokaun, A.; Sager, W.; Eicke, H.-F. *J. Colloid Interface Sci.* **1992**, *148*(1), 80.

(10) Kumar, P.; Pillai, V.; Bates, S. R.; Shah, D. O. *Mater. Lett.* **1993**, *16*, 68.

(11) Mazdhyasni, K. S.; Dolloff, R. T.; Smith, J. S. *J. Am. Ceram. Soc.* **1969**, *52*(10), 523.

(12) Nitsche, R. *Helv. Phys. Acta* **1958**, *31*, 306.

(13) Marks, O.; Günter, J. R.; Hofer, F. *React. Solids* **1988**, *6*, 217.

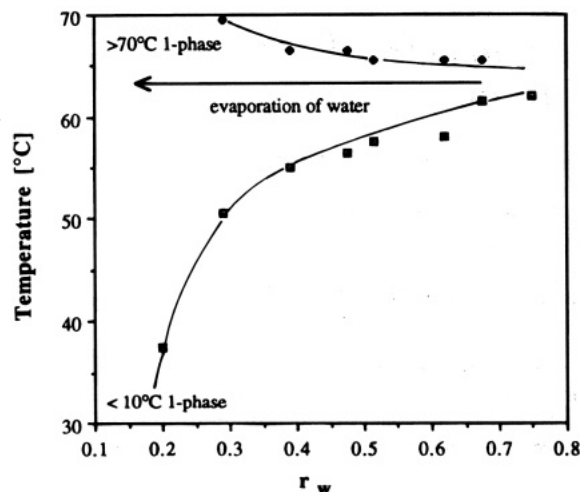


Figure 1. Phase diagram of Genapol OX 30/decane/water. The area between the connected points is the one-phase region of the pure microemulsion. r_w denotes mass fraction of water and surfactant. During evaporation one moves along the arrow. Supersaturation and successive precipitation of the TGS crystals take place inside nanodroplets.

size by scanning electron microscopy was not possible. The powder was repeatedly washed with acetone, centrifuged, and freeze-dried.

BaTiO₃ Synthesis. *a. Microemulsion/oxalate Route.* As starting materials, BaCl₂·2H₂O (puriss. p.a., Fluka), TiCl₄ (puriss. p.a., Fluka) and oxalic acid (H₂C₂O₄) (puriss. p.a., Fluka) were used. Water was deionized and distilled, and oil (decane) and commercial grade surfactant (Genapol OX 30, Hoechst) were used as described above.

Due to the hydrophilic character of TiCl₄, the desired volume was placed in a vessel in a glovebox under nitrogen. Water and BaCl₂ were quickly added to achieve a stoichiometric 0.05 M solution of both components. This aqueous solution was quickly dissolved in the oil/surfactant mixture, before the titanium hydroxide could form aggregates too large for the nanodroplets. This procedure produced a transparent microemulsion. In a second microemulsion, a 0.1 M oxalic acid solution formed the aqueous phase. All other components were kept constant. These two microemulsions (ME's) were mixed under stirring at a temperature where both ME's were stable. During this procedure, the ME and the droplet size remained stable. Precipitation occurs when two droplets of different contents collide and mix their contents. After half an hour, the mixture (still one phase and transparent) was centrifuged. The centrifugate was repeatedly washed and centrifuged as described for TGS and freeze-dried. A part of the powder was taken for electron microscopy and X-ray measurements, and the other part was calcinated at different temperatures.

b. Hydrolysis of the Alkoxides. Barium (puriss. p.a., Fluka) was dissolved in dried and freshly distilled ethanol (purum,

Fluka). No complete solution could be achieved despite refluxing for 24 h under nitrogen. This was possibly due to barium hydroxide which was either attached to the barium or was formed with traces of water in the reaction vessel. Stoichiometric amounts of titanium tetraethanolate were added to the boiling mixture (bp ethanol 78–80 °C) under vigorous stirring. Hydrolysis was achieved by quickly adding 80 mL of twice distilled water. The supernatant solvent was distilled off, and a white powder remained, which was freeze-dried. The powder was heated stepwise to achieve different grain sizes.

Electron Microscopy (EM). For transmission electron microscopy (TEM; Zeiss CM-10), the sample was prepared by putting a drop of the mixed ME's on a Formvar/copper net and drying at ambient temperature.

For conventional scanning electron microscopy, the TGS powders were put on double-sided adhesive tape mounted on an aluminum specimen setup. Residual powder was blown from the tape with nitrogen. The TGS was sputtered with 10 nm gold in a high-vacuum sputter coater (BAL-TEC, MED 020). The conventional scanning electron microscopy (SEM) was performed on a Philips SEM 515.

For field emission scanning electron microscopy (FESEM), the powder samples were prepared as described for the TGS samples and sputtered with 3 nm platinum in place of gold. FESEM was performed on a JEOL JSM 6300 F microscope.

X-ray Diffraction. For the TGS powders, X-ray diffraction was performed with a Guinier camera using Fe K α X-rays. The samples were prepared by placing the powder on a sticky tape. The BaTiO₃ powders were measured in a diffractometer (Siemens DIFFRAC 500) using Cu K α X-rays. Aluminum or plastic sample holders were used. All measurements were performed at room temperature.

Results and Discussion

The X-ray results from samples TGS 1–3 are shown in Figure 2. The observed lines are consistent with the data of JCPDS-ICDD file 14-873. The SEM micrographs of the powders are shown in Figures 3–5a. Figures 3–5b show the respective size distributions which were determined by measuring and counting the particles of a micrograph showing at least 150 particles.

The crystals obtained were much larger than the amount of the TGS dissolved in one droplet. Their size is inversely proportional to the initial droplet size. A detailed study of the ME by dynamic light scattering measurements revealed that an increase of the electrolyte concentration forces the droplets to form agglomerates. Regarding the final size of the particles, it is conceivable that the whole TGS, contained in an agglomerate of droplets, takes part in the building of one crystallite. There is no indication that the particles consist of smaller subunits, neither from the electron micrographs nor from broadening of the diffraction lines.

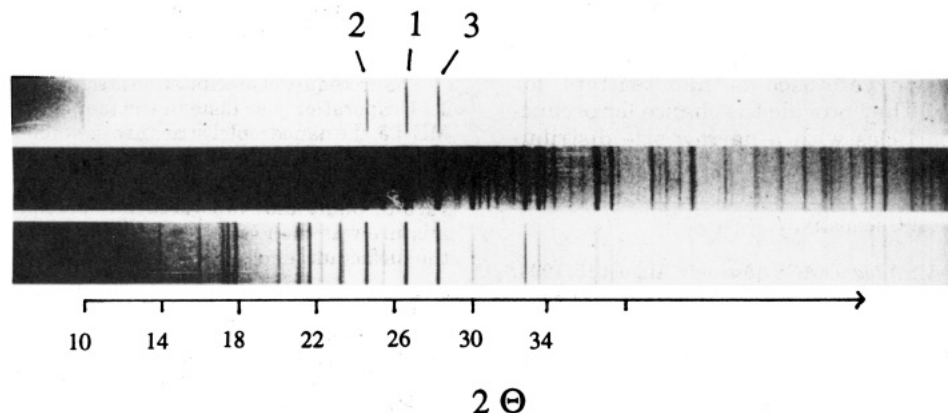


Figure 2. X-ray analysis of the TGS powders (top, TGS 1; middle, TGS 2; bottom, TGS3). The three strongest lines 1–3 are indexed with increasing intensity, according to JCPDS-ICDD file 14-873. Line 1 corresponds to the hkl values -131 ; lines 2 and 3 correspond to the hkl values -220 and 040 , respectively.

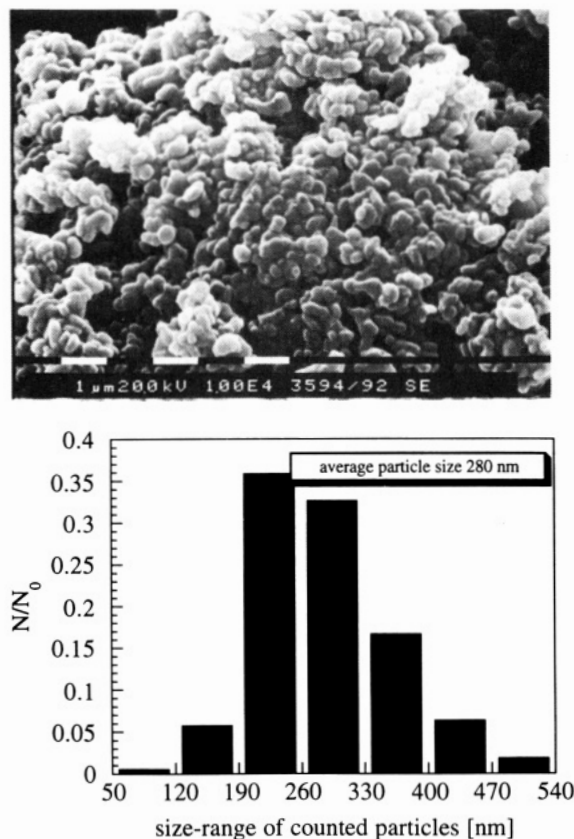


Figure 3. (a, Top) SEM micrograph of sample TGS 1. (b, Bottom) Size distribution of sample TGS 1; N_0 denotes the total number of measured and counted particles and N the number of particles in a given size range. The range is indicated on the scale at the bottom of the figure.

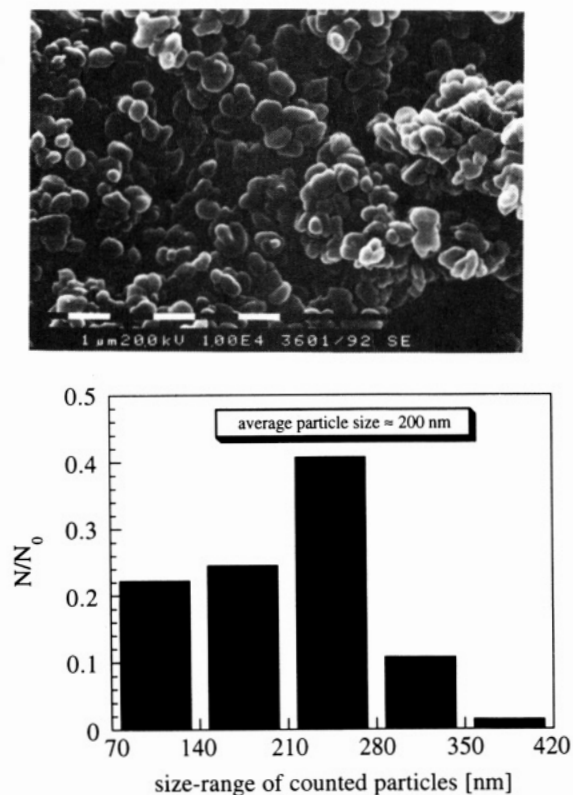


Figure 4. (a, Top) SEM micrograph of sample TGS 2. (b, Bottom) Size distribution of sample TGS 2.

For the preparation of BaTiO_3 using the microemulsion/oxalate technique, we found that the diffraction lines of

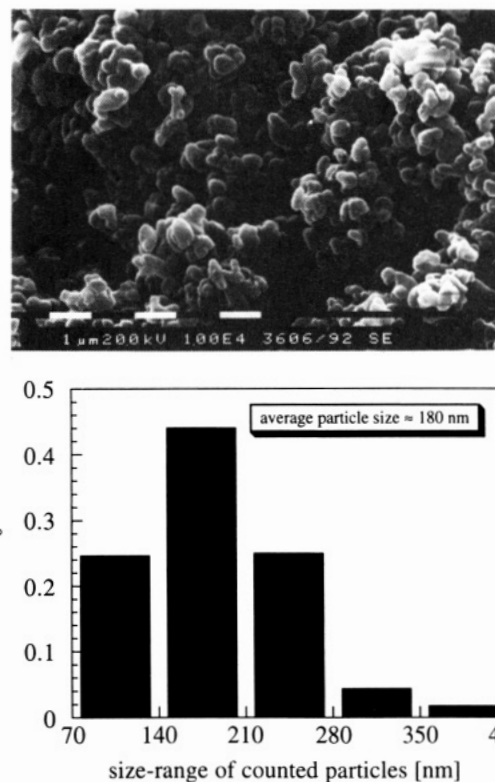


Figure 5. (a, Top) SEM micrograph of sample TGS 3. (b, Bottom) Size distribution of sample TGS 3.

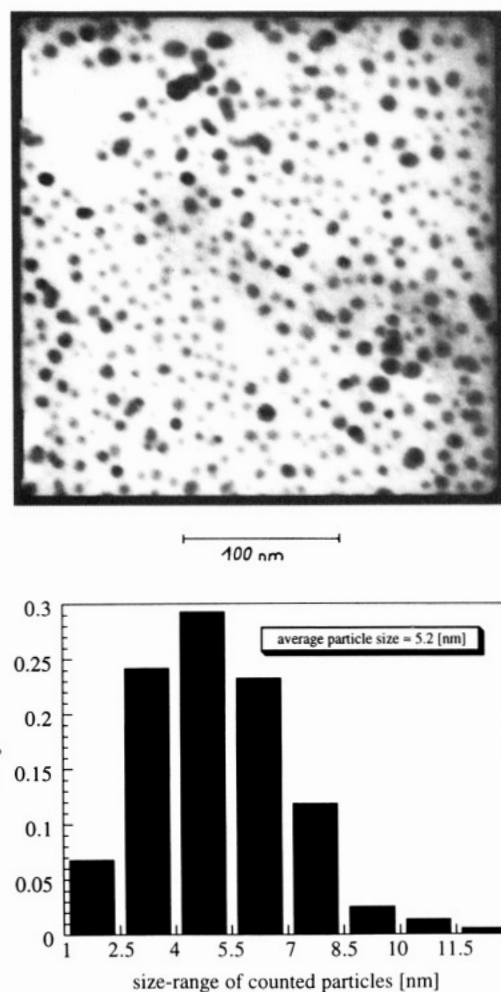


Figure 6. (a, Top) TEM micrograph of the barium-titanium oxalate powder precipitated from ME. (b, Bottom) Size distribution of the precipitated oxalate.

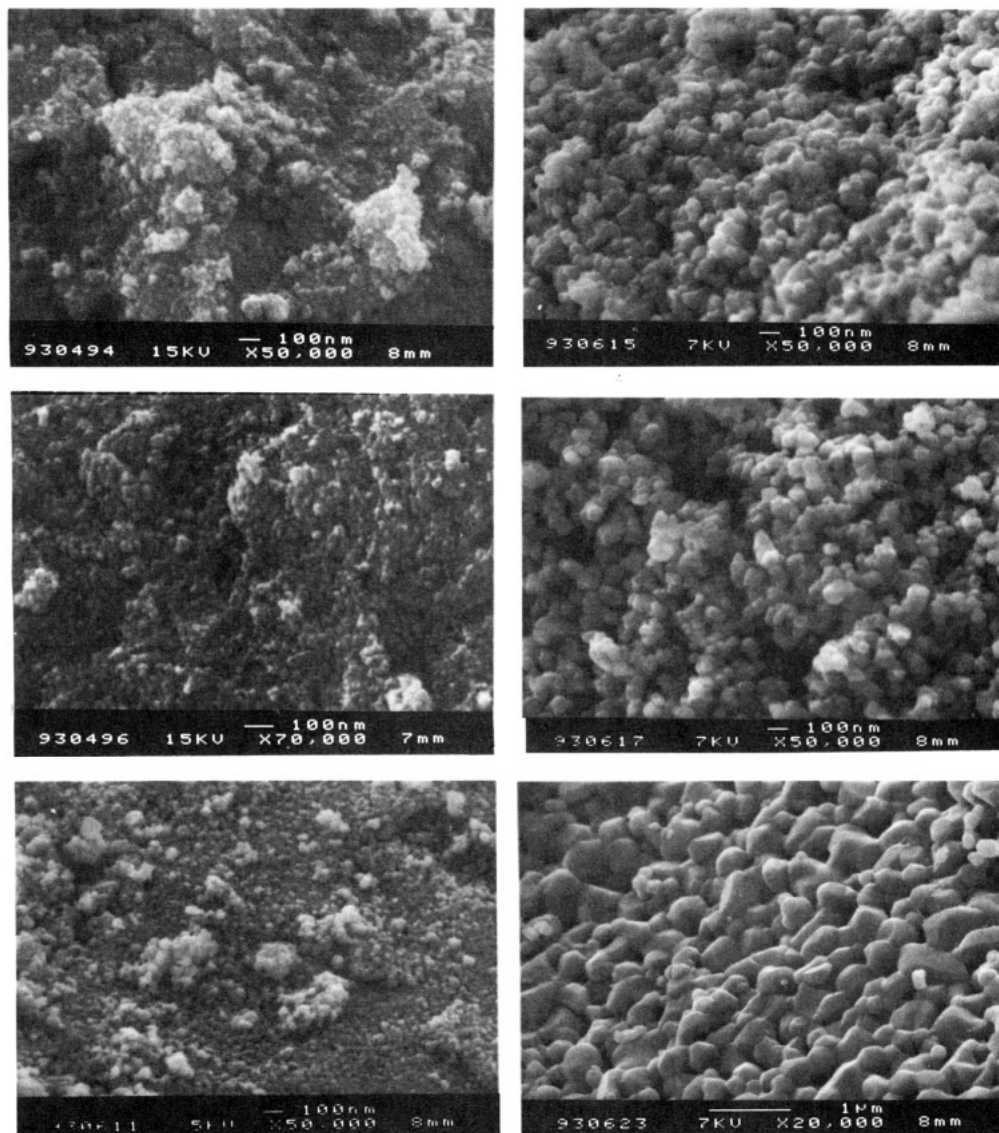


Figure 7. FESEM micrographs of the freeze-dried BaTiO_3 treated at different conditions: (a, top left) without further treatment; (b, middle left) 200 °C for 24 h; (c, bottom left) 400 °C for 24 h; (d, top right) 600 °C for 24 h; (e, middle right) 800 °C for 24 h; (f, bottom right) 1000 °C for 24 h.

the X-ray analysis were not in accordance with the data described for the Ba, Ti oxalate hydrate in the JCPDS-ICDD file.

The size and size distribution of the precipitate according to TEM are shown in Figure 6a,b.

Calcination of the powder was carried out at different temperatures (from 400 to 1200 °C) and for different periods of time up to 24 h. With increasing temperature we observed an increase in particle size. The X-ray measurements showed that a pure BaTiO_3 phase could not be achieved. At lower temperatures, the impurities could not be identified except for BaCO_3 . The experiments were repeated several times, however, with similar results.

Very satisfying results were obtained for the preparation of BaTiO_3 by hydrolysis of the alkoxides.

The X-ray diffraction peaks of the freeze-dried powders are in good agreement with the values reported for pseudocubic BaTiO_3 (JCPDS-ICDD file 31-174), as can be seen from Figure 8. In the case of the BaTiO_3 powder heated up to 1000 °C, the peak values are in accordance with data reported for the tetragonal phase (JCPDS-ICDD 5-626). The peaks of the powders which were treated at lower temperatures are found intermediate between the values of these two phases. In no case were impurities seen from the diffractograms.

The particle size is shown in the FESEM micrographs of Figure 7a–f. FESEM was used instead of conventional SEM because of better resolution due to the fact that a smaller diameter of the electron beam can be realized. Hence, a good resolution was achieved even in the cases of the smallest crystallites (10 nm).

To the best of our knowledge, this is the first time that a broad range of different crystallite sizes, starting from very small particles, could be attained in the case of BaTiO_3 . This system should accordingly be particularly suitable for the applications mentioned in the Introduction (i.e. for the production of ceramics and nanocomposite materials).

Conclusions

Evaporation of nanosize droplets of a microemulsion proved to be a suitable method for the precipitation of submicrometer crystallites. However, the size of the crystallites is not determined by the amount of substance dissolved in one droplet, as might be expected from the schematic picture of the process (Figure 1). Apart from exchange processes between the droplets, which are known

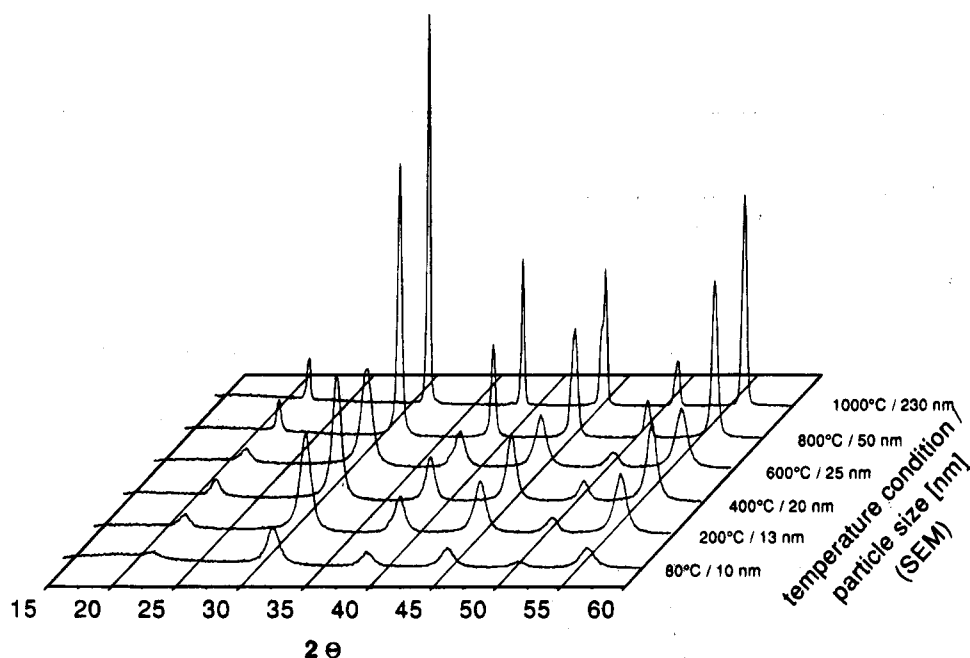


Figure 8. X-ray diffractograms of the BaTiO_3 produced by hydrolysis of the ethanlates and successive heating.

from other emulsion precipitation techniques,¹⁴ we found another mechanism (aggregation) which prevents simple control of the particle size. Aggregation of the droplets, which occurs at higher electrolyte concentrations, leads to a remarkable increase toward the expected crystallite size.

In the case of the BaTiO_3 synthesis, precipitation of the mixed oxalates by microemulsion (ME) was not successful. The main reason might be the inability to dissolve the titanium homogeneously, because the ME is not stable at low pH conditions. Also, the surfactant at the surface of the precipitate and the chlorine counterions lead to impurities during the heat treatment.

A successful procedure for the synthesis of pure nanometer-sized BaTiO_3 particles is the fast hydrolysis of mixed ethanlates. Furthermore, finely grained precipi-

tates and larger sized particles in the submicrometer range can be produced by suitable heat treatment. The size distribution remains remarkably narrow in the course of such a treatment.

The BaTiO_3 powders as well as the TGS powders produced by the described methods are suitable for investigations of size effects in ferroelectric materials due to their small sizes, their purity, and their narrow size distributions. They also offer the chance for homogeneous dispersions in liquids or in polymer media.

Acknowledgment. We thank Y. Hauger for the determination of the phase diagrams, H.-P. Lang, J. P. Ramseyer, and Prof. Graeser for recording the X-ray measurements, and M. Düggelin and R. Colombo for SEM measurements. The authors also thank Prof. J. R. Günter and Dr. P. Keusch for valuable suggestions concerning the preparation of BaTiO_3 , and last but not least, we wish to acknowledge financial support from the Swiss National Science Foundation.

(14) Sager, W.; Sun, W.; Schwarz, U. D.; Eicke, H. F. *Progr. Colloid Polym. Sci.* **1993**, 93, 348.

(15) Sager, W.; Eicke, H. F.; Sun, W. *Colloids Surf. A: Physicochem. Eng. Aspects* **1993**, 79, 199.