Available online at www.sciencedirect.com

SCIENCE DIRECT®

Journal of the European Ceramic Society 23 (2003) 127–132

www.elsevier.com/locate/jeurceramsoc

Phase content, tetragonality, and crystallite size of nanoscaled barium titanate synthesized by the catecholate process: effect of calcination temperature

Wongduan Maison[a], Reinhard Kleeberg[b], Robert B. Heimann[b,*], Sukon Phanichphant[a]

[a]Department of Chemistry, Faculty of Science, Chiang Mai University, Chiang Mai 50200, Thailand
[b]Department of Mineralogy, Freiberg University of Mining and Technology, D-09596 Freiberg, Germany

Received 17 August 2001; received in revised form 11 February 2002; accepted 3 March 2002

Abstract

A modified catecholate process has been applied to synthesize high purity barium titanate powders in the submicron range. A barium titanium-catechol complex, $Ba[Ti(C_6H_4O_2)_3]$ was prepared from $TiCl_4$, $C_6H_4(OH)_2$ and $BaCO_3$, freeze-dried, and calcined for 3 h at temperatures between 600 and 1300 °C. Phase transformation and crystallite size of the calcined powders were investigated as a function of the calcination temperature by X-ray diffraction methods, and particle morphology and size were studied by scanning electron microscopy. With increasing calcination temperature, $BaTiO_3$ transformed from the (pseudo)cubic to the ferroelectric tetragonal phase. The tetragonality (c/a-1) increases with increasing calcination temperature and increasing crystallite size, respectively. Higher temperatures clearly favoured particle growth and the formation of large and hard agglomerates. The crystallite size of the tetragonal phase increased from <60 nm at 600–800 °C to 1237 ± 344 nm at 1300 °C.

Keywords: $BaTiO_3$; Calcination; Phase development; Powders-chemical preparation

1. Introduction

Barium titanate is a common ferroelectric material with a high dielectric constant, widely utilized to manufacture electronic components such as multilayer capacitors (MLCs),[1,2] PTC thermistors,[3–6] piezoelectric transducers,[7,8] and a variety of electro-optic devices.[1,9] Conventionally, barium titanate has been synthesized by a solid-state reaction between $BaCO_3$ and TiO_2.[10–12] The overall reaction involves the initial formation of $BaTiO_3$ at $BaCO_3/TiO_2$ grain boundaries which then reacts with $BaCO_3$ resulting in the formation of Ba_2TiO_4. Finally, formation of $BaTiO_3$ was obtained by reaction between Ba_2TiO_4 and TiO_2 at optimum conditions. During this reaction, precise control of stoichiometry and powder characteristics are difficult to maintain because of lack of consistency in raw material sources and local inhomogeneities arising from incomplete mixing and reaction of the constituents. The high calcination temperatures needed for this reaction to occur often result in the formation of coarse aggregates which can be difficult to disperse or reduce during subsequent milling. To overcome these deficiencies, alternative methods of powder synthesis have been developed and described by many authors such as co-precipitation of oxalates,[13–16] citrates,[17–19] catecholate[20–22] and others.[23–27] Most of these techniques take advantage of reactions that favour the homogeneous distribution of barium and titanium on an almost atomic scale in the solution so that the same distribution is largely maintained also in the precipitates. The immediately adjacent ions of barium and titanium can therefore react with each other at relatively low temperature to form homogeneous and stoichiometric barium titanate.

It is well known that the physical properties of ceramics are very sensitive to their microstructure. Hence, it is essential to control the properties of the initial barium titanate powder when producing ceramics with dense, uniform and fine-grained microstructure.[28] Carbone and Reed[29] have shown that the particle size distribution and agglomerate structure of the starting powders have an important influence on the microstructure

---

* Corresponding author. Tel.: +49-3731-39-2666; fax: +49-3731-39-3129.

E-mail address: heimann@mineral.tu-freiberg.de (R. B. Heimann).

PII: S0955-2219(02)00071-7

achieved in $BaTiO_3$. Hence it is mandatory to control the particle size distribution in the powder to obtain dense ceramics with uniform grain size after sintering and to formulate barium titanate powders with precisely controlled composition in addition to controlling the particle morphology. In this paper, we focus on the effect of the calcining temperature on phase composition and microstructural evolution of barium titanate fine powders synthesized by the catecholate process.

2. Materials and methods

2.1. Sample preparation

Barium titanate was synthesized according to a modified catecholate process.[21] Catechol [1, 2-dihydroxybenzene, $C_6H_4(OH)_2$] was added to dry toluene and heated to boiling to dissolve the catechol reagent. A solution of $TiCl_4$ in dry toluene was then added dropwise. The dark red $H_2[Ti(C_6H_4O_2)_3]$ precipitate formed was isolated by filtration, washed with hot toluene, and dried. Then it was gradually added to a boiling suspension of $BaCO_3$. The $Ba[Ti(C_6H_4O_2)_3]$ complex was obtained as an aqueous solution that was freeze-dried and subsequently calcined for 3 h at temperatures between 600–1300 °C.

2.2. Sample characterization

X-ray diffractometry (URD-6, Seifert-FPM, Germany) with CoK_α radiation was used to determine lattice parameters, crystallite size and tetragonality. Rietveld refinement was carried out to determine the quantitative composition of the phases formed during the calcination process. Tetragonality was determined using a D 5000 (Siemens) instrument and CuK_α radiation. Quantitative phase analysis, mean crystallite diameter and the isotropic microstrain parameter were provided by the BGMN Rietveld program software[30] using the fundamental parameter peak shape model. Contributions of wavelength distribution, geometrically caused peak shape, and sample real structure were convoluted as sums of Lorentzian and squared Lorentzian functions. The instrumental/geometrical part was calculated by a raytracing procedure. For the sample function a crystallite size broadening approach was implemented.[30] This model can calculate the mean crystallite diameter of sharp log-normal size distributions quite common in ceramic materials. However, this model describes only the size of volume units in which the X-ray radiation is scattered coherently. The isotropic microstrain parameter used as the second part of the real structure model was derived from the width of a d^{-2}-squared Lorentzian function. Stable refinement of the lattice parameters of the tetragonal phase was difficult in presence of the dominating cubic phase at lower calcination temperatures. For the 600 °C product the tetragonality of the assumed t-$BaTiO_3$ could not be refined with certainty. However, in contrast to the approach by Beck et al.[34] the Rietveld method constrains the intensities of the hkl interplanar spacings. Hence, profile fitting of strongly overlapping lines is more stable and allows in the other cases for the determination of mean size and microstrain parameters of 'pseudo'cubic and tetragonal $BaTiO_3$ simultaneous with phase composition and lattice parameters. Nevertheless, the reliability of the results is restricted to the simple model of two (cubic and tetragonal) phases having individual but nearly homogenous microstructures. This simplification supports at least qualitatively the models discussed below in Section 3.1.

Scanning electron microscopy (Jeol JSM-840A, Japan) was employed to investigate morphology and particle size of the powders. Before coating with a thin gold layer, particle agglomerates were broken up by sonification.

3. Results and discussion

3.1. Phase transformation

Fig. 1 shows the X-ray diffraction pattern of $BaTiO_3$ derived from a catechol precursor complex by heat treatment for 3 h between 600 and 1300 °C. The most intense reflections appearing in the majority of the XRD pattern indicate the formation of a barium titanate phase with alleged cubic symmetry below a calcination temperature of about 900 °C. At higher temperatures transformation into a phase with tetragonal symmetry occurs that is apparent by the splitting of the single 200 interplanar spacing at about $2\theta = 53°$ CoK_α into a 002/200 doublet. At the lowest calcination temperature employed a very broad low intensity peak was observed at about $2\theta = 31°$ CoK_α that could not be assigned to any phase listed in the ICDD PDF-2. It was tentatively concluded that a more or less amorphous product was formed related to an incompletely decomposed metalorganic complex. The doublet around $2\theta = 28°$ CoK_α and some lines near 40, 49 and 55°, observed at the lowest calcination temperatures, could be clearly assigned to (residual) $BaCO_3$ (witherite).

The intensity ratios of the modeled peaks were compared to the values given in ICDD PDF-2 (file numbers 31-174 and 5-626 for the paraelectric cubic and the ferroelectric tetragonal $BaTiO_3$, respectively). The lattice parameters were given as $a_0 = 399.4$ pm and $c_0 = 403.8$ pm for the tetragonal form and $a_0 = 403.1$ pm for the cubic form.[31] In our experiments, the lattice parameters calculated from the diffraction data indicate that the tetragonalities ($c/a-1$) are 0.782% ($a_0 = 399.81$ pm, $c_0 =$ 402.9 pm) at 900 °C, 0.863% ($a_0 = 399.73$ pm,

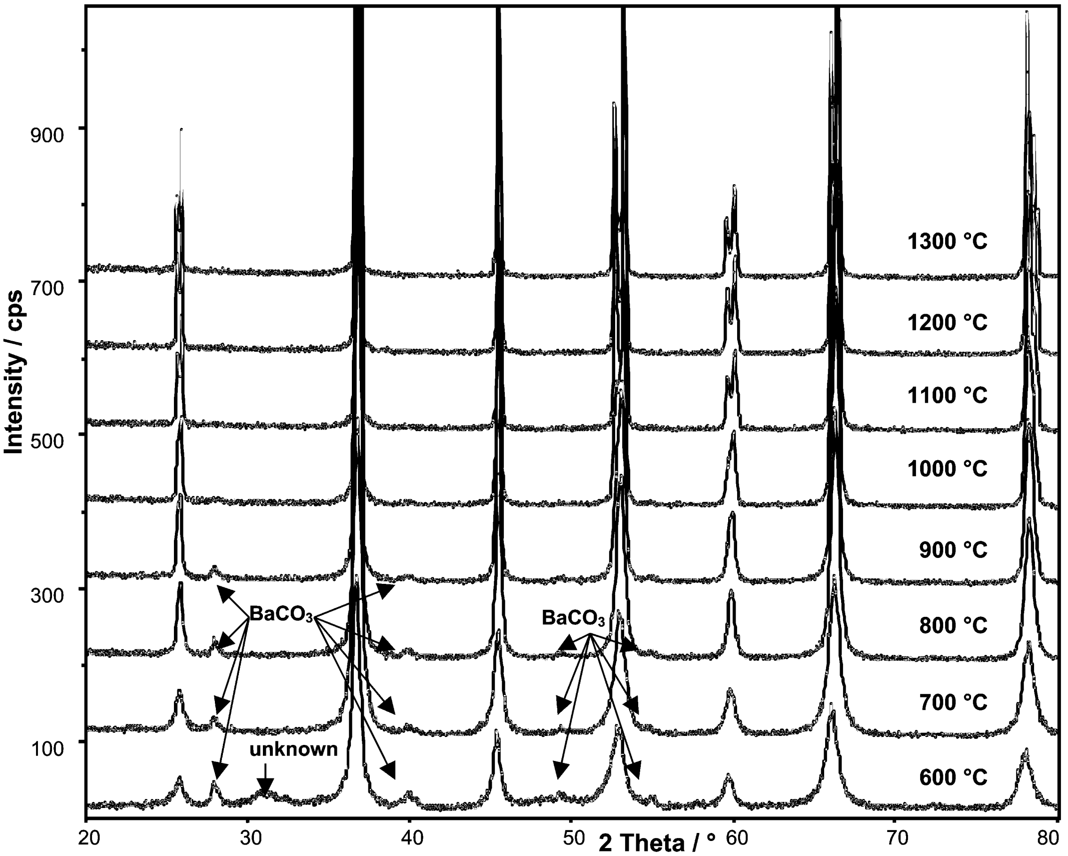


Fig. 1. XRD powder pattern of $BaTiO_3$ calcined at various temperatures with a constant dwell time of 3 h. The radiation used was CoK_α.

$c_0 = 403.18$ pm) at 1000 °C, and 0.976%($a_0 = 399.45$ pm, $c_0 = 403.35$ pm) at 1100 °C for the tetragonal phase, and $a_0 = 401.0$ pm for the cubic phase. As the c/a ratio of $BaTiO_3$ has been shown to decrease with decreasing particle size[32] reduction of tetragonality ($c/a-1$) results eventually in the occurence of a so-called 'superpara-electric' phase at grain size below 100 nm.[33]

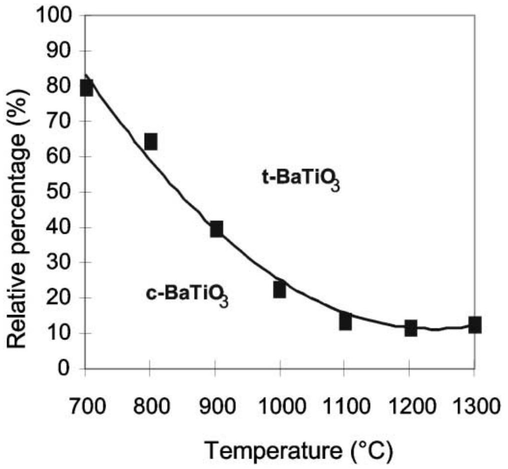


Fig. 2. Dependence of the cumulative percentages of cubic and tetragonal barium titanate on calcination temperature.

The thermal transition of the metastable c-$BaTiO_3$ to t-$BaTiO_3$ is shown in Fig. 2. The relative percentages were obtained from quantitative data provided by the Rietveld refinement. Even at calcination temperatures beyond 1100 °C there is still an appreciable contribution of the cubic phase. In Fig. 3 it is shown that the

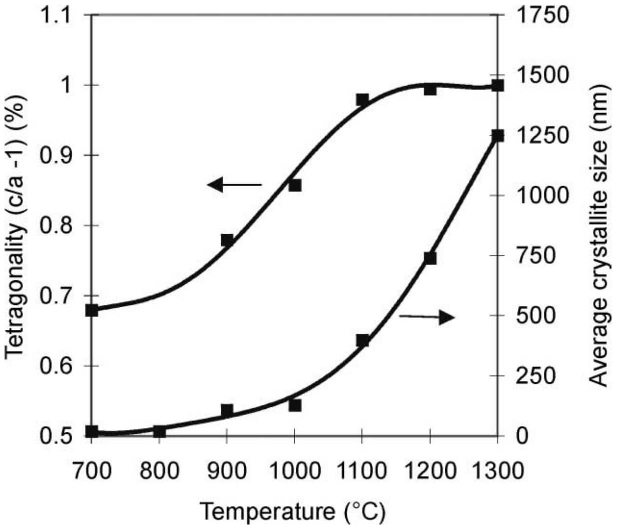


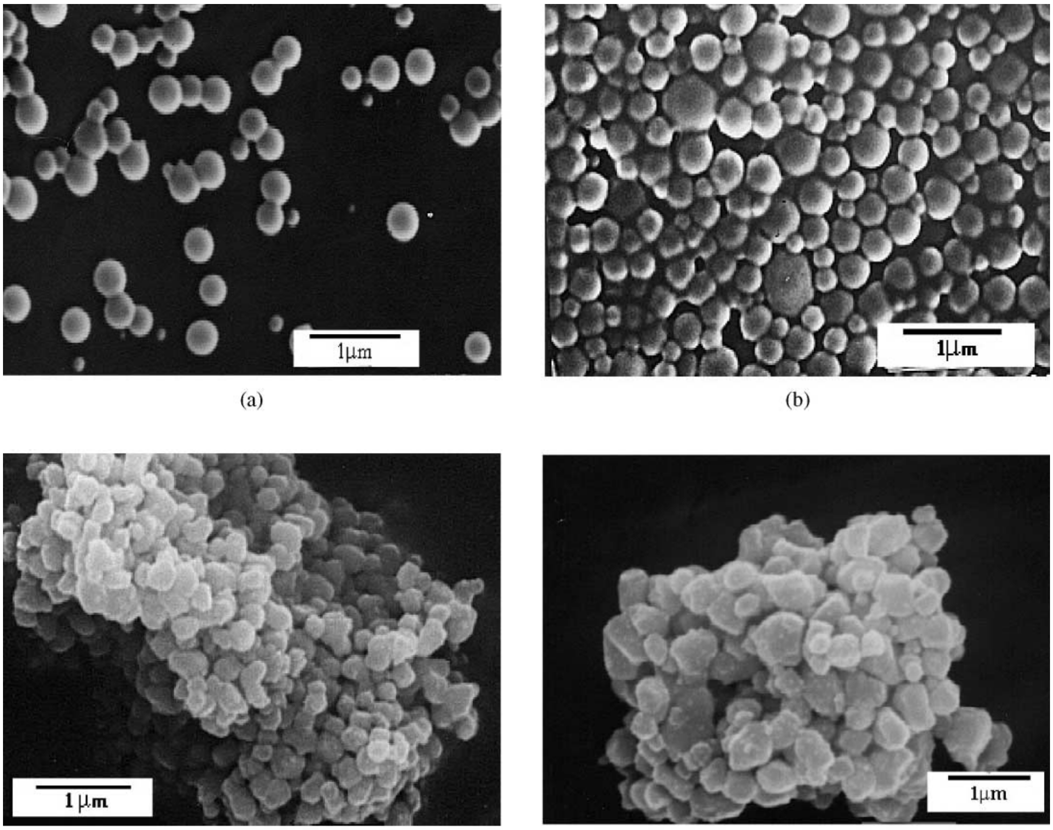
Fig. 3. Tetragonality ($c/a-1$) and crystallite size of barium titanate as a function of calcination temperature.

tetragonality ($c/a-1$) increases with increasing calcination temperature[34] as does the XRD crystallite size determined by an isotropic size model for which calculation the microstrain was confined to zero.

Particle size dependence of the tetragonal lattice deformation in $BaTiO_3$ powders with particle diameters between 0.5 and 1.5 μm has been reported by Arlt et al.[33] Below 0.5 μm, the existence of the pseudocubic or even the cubic phase has been suggested. Along this line, Uchino et al.[32] and Yen et al.[35] showed that the c/a ratio decreases with decreasing particle size, in good agreement with this work. Cubic to tetragonal transformation occurs with increasing particle size.

The reason barium titanate occurs at low calcination temperature in the paraelectric cubic instead of the ferroelectric tetragonal structure has been tentatively explained by Samara[36] as being caused by microstress inside the small particles that appear as a result of clustering into larger aggregates. However, Li and Shi[37] pointed out that these stresses ought to be compressive rather than tensile, and thus would favour the formation of the denser, i.e. the cubic phase at higher calcination temperature. Instead, they conjecture that a reduction of the depolarization energy in clustered barium titanate powders due to a multidomain state shifts the tetragonal towards the cubic structure. A similar mechanism was discussed previously by Kniepkamp and Heywang.[38]

A rather unconstrained explanation for the symmetry reversal can be given considering the 'mesoscale' twinning mode associated with a ferroelastic phase transition.[39] Between twin walls ferroelastic domains generate a highly non-linear elastic response characterized by the mechanical switching between two preferred orientation states of barium titanate, the cubic structure with paraelastic and the tetragonal structure with ferroelastic properties. If switching is suppressed by domain wall pinning the distorted phase is co-elastic and the pinning energy density is closely related to the Peierls energy.[40] Typical twin wall widths in barium titanate are 4–10 times the crystallographic repetition length normal to the 180° twin plane (101).[41] With a lattice constant of about 0.4 nm this width is about 6 nm showing that the twin walls are not sharp but diffuse. On the other hand the distances between twin boundaries, i.e. domain sizes are, among others, a function of the calcination temperature as shown in Fig. 3. Below a critical domain size of 270 nm[39] the crystal grains are untwinned and appear (pseudo)cubic without a split into the 002/200 doublet. This has been modeled by calculating in a kinematic



(a) (b)
(c) (d)

Fig. 4. SEM micrographs of $BaTiO_3$ powders calcined for 3 h at (a) 700, (b) 900, (c) 1000C, and (d) 1100 °C.

approach the scattered X-ray intensities of a crystal divided into domains by parallel coherent twin boundaries on a (101) plane.[42] With decreasing average crystallite size the 002/200 doublet transforms into a broad single 200 peak whose width decreases as the crystallite size is further reduced. Hence, the appearance of an alleged cubic structure at low calcination temperature corresponding to a small grain size below 60 nm with a low tetragonality value (Fig. 3) is a consequence of the microdomain size, the dispersion of twin width distribution, as well as the twin wall width. In conclusion, our results appear to be consistent with the model developed by Salje.[39]

3.2. Morphology and particle size of calcination products

SEM micrographs of $BaTiO_3$ powders calcined at four different temperatures are shown in Fig. 4a–d.

The low temperature calcination product at 700 °C (Fig. 4a) shows spherical particles of about 200 nm diameter. This is much larger than the crystallite size determined by XRD (Fig. 3) suggesting an internal structure of the particles consisting mainly of a (pseudo)cubic phase and twinned domains as discussed above. At 900 °C (Fig. 4b) and 1000 °C (Fig. 4c) there is evidence of exaggerated grain growth with the development of interparticle necks and consequently particle fusion, and also for an increase in particle size corresponding to cube-shaped forms.

With increasing calcination temperature the particles lose their spherical morphology, and at 1100 °C (Fig. 4d) the product consists of irregularly shaped crystallite agglomerates of about 200–500 nm. The (volume weighted) domain size of the dominating tetragonal phase (392 nm, Fig. 3) determined by XRD supports the SEM findings and appears to be consistent with monodomain crystalline particles.

4. Conclusion

A modified catecholate process has been developed to synthesize high purity $BaTiO_3$ fine powders with a high degree of reproducibility. Using a combination of XRD Rietveld refinement and SEM techniques, the effects of the calcination temperature on phase transformation, tetragonality, and particle size of $BaTiO_3$ were examined. At low calcination temperature the dominating phase is cubic. This has been tentatively explained by a model considering the mesoscale twinning mode associated with a ferroelastic phase transition. With increasing calcination temperature the crystallite size of the ferroelectric tetragonal phase increases, and the particle morphology changes from spherical to acicular with cube-shaped particles dominating.

Acknowledgements

Financial support from The National Metal and Materials Technology Center (MTEC) and The National Science and Technology Development Agency (NSTDA) are gratefully acknowledged. One of the authors (RBH) thanks the Deutscher Akademischer Austauschdienst (DAAD) for sponsoring a teaching and research sojourn at the Departments of Chemistry and Physics, Chiang Mai University, Thailand during which parts of this paper were written. The authors are indebted to Prof. Heywang and Dr. Thomann, Siemens AG, Corporate Research, München, Germany for critical comments.

References

1. Moulson, A. J. and Herbert, J. M., *Electroceramics: Materials Properties and Applications*. Chapman and Hall, London, 1990.
2. Mostaghaci, H. and Brook, R. J., Microstructure development and dielectric properties of fast-fired $BaTiO_3$ ceramics. *J. Mater. Sci.*, 1986, **21**, 3575.
3. (a) Heywangm, W., Barium titanate as a PTC thermistor. *Solid-State Electr.*, 1961, **3**, 51; (b) Semiconducting barium titanate. *J. Mater. Sci.*, 1971, **6**, 1214.
4. Heywang, W., Resistivity anomaly in doped barium titanate. *J. Am. Ceram. Soc.*, 1964, **47**, 484.
5. Jonker, G. H., Some aspects of semiconducting barium titanate. *Solid-State Electr.*, 1964, **7**, 895.
6. Huybrechts, B., Ishizaki, K. and Takata, M., The positive temperature coefficient of resistivity in barium titanate. *J. Mater. Sci.*, 1995, **30**, 2463.
7. Bechman, R., Elastic, piezoelectric and dielectric constants of polarized barium titanate ceramics and some applications of the piezoelectric equations. *J. Acoust. Soc. Amer.*, 1956, **28**, 347.
8. Ohara, Y., Koumoto, K. and Yanagida, H., Barium titanate ceramics with high piezoelectricity fabricated from fibrous particles. *J. Am. Ceram. Soc.*, 1985, **68**, C-108.
9. Smolenskii, G. A., *Ferroelectrics and Related Materials*. Gordon and Breach, New York, 1984.
10. Templeton, L. K. and Pask, J. A., Formation of $BaTiO_3$ from $BaCO_3$ and TiO_2 in air and in CO_2. *J. Am. Ceram. Soc.*, 1959, **42**, 212.
11. Beauger, A., Mutin, J. C. and Niepce, J.-C., Role and behaviour of orthotitanate Ba_2TiO_4 during the processing of $BaTiO_3$ based ferroelectric ceramics. *J. Mat. Sci.*, 1984, **19**, 195.
12. Niepce, J.-C. and Thomas, G., About the mechanism of the solid-way synthesis of barium metatitanate-industrial consequences. *Solid State Ionics*, 1990, **43**, 69.
13. Clabaugh, W. S., Swiggard, E. M. and Gilchrist, R., Preparation of titanyl oxalate tetrahydrate for conversion to barium titanate of high purity. *J. Res. Natl. Bur. Stand. U.S.*, 1956, **56**, 289.
14. Gallagher, P. K. and Schrey, F., Thermal decomposition of some substituted barium titanyl oxalates and its effect on the semiconducting properties of the doped materials. *J. Am. Ceram. Soc.*, 1985, **46**, 567.
15. Virkar, A. N. and Sundaram, S. K., Studies on the effect of minor glass additives on the sintering and dielectric properties of barium titanate. *Trans. Indian Ceram. Soc.*, 1985, **44**, 71.
16. Lin, T.-F. and Hu, C.-T., Influence of stoichiometry on the microstructure and positive temperature coefficient of resistivity of semiconducing barium titanate ceramics. *J. Am. Ceram. Soc.*, 1990, **73**, 531.
17. Fang, T.-T. and Lin, H.-B., Factors affecting the preparation of barium titanyl oxalate tetrahydrate. *J. Am. Ceram. Soc.*, 1989, **72**, 1899.

18. Rajendran, M. and Rao, M. S., Formation of $BaTiO_3$ from citrate precursor. *J. Solid State Chem.*, 1994, **113**, 239.
19. Hennings, D. and Mayr, W., Thermal decomposition of (BaTi) citrates into barium titanate. *J. Solid State Chem.*, 1978, **26**, 329.
20. Ali, N. J. and Milne, S. J., Synthesis and properties of barium titanate powder derived from a catechol complex. *Brit. Ceram. Trans. J.*, 1987, **86**, 113.
21. Ali, N. J., Bultitude, J., Xue, L. and Milne, S. J., Ceramic processing characteristics of $BaTiO_3$ powder prepared from a catecholate precursor. *Brit. Ceram. Proc.*, 1989, **41**, 29.
22. Ali, N. J., Bultitude, J., Xue, L. A. and Milne, S. J., Preparation of stoichiometric M/TiO_3 powders ($M/=Ba$, Sr, Ca) from catecholate complexes. *Mat. Res. Soc. Symp. Proc.*, 1988, **121**, 269.
23. Mazdiyasni, K. S. and Brown, L. M., Synthesis of Nb_2O_5-doped $BaTiO_3$ with improved electrical properties. *J. Am. Ceram. Soc.*, 1972, **55**, 633.
24. Kirby, K. W., Alkoxide synthesis techniques for $BaTiO_3$. *Mat. Res. Bull.*, 1988, **23**, 881.
25. Chaput, F. and Boilot, J. P., Chemical processing of (Ba, Sr)(Ti, Zr)O_3 perovskite ceramics. *J. Mater. Sci. Lett.*, 1987, **6**, 110.
26. Vivekanandan, R., Philip, S. and Kutty, T. R. N., Hydrothermal preparation of Ba(Ti, Zr)O_3 fine powders. *Mat. Res. Bull.*, 1986, **22**, 99.
27. Abe, K., Aoki, M., Rikimaru, H., Ito, T., Hidaka, K. and Segawa, K. *Process for Processing a Composition which Includes Perovskite Compounds*. US Patent No. 4,643,984, 17 February, 1987.
28. Yan, M. F., Microstructural control in the processing of electronic ceramics. *Mat. Sci. Eng.*, 1981, **48**, 53.
29. Carbone, T. J. and Reed, J. S., Microstructure development in barium titanate: effects of physical and chemical inhomogeneities. *Am. Ceram. Soc. Bull.*, 1979, **58**, 512.
30. Bergmann, J., Kleeberg, R., Haase, A. and Breidenstein, B., Advanced fundamental parameters model for improved profile analysis. *Mat. Sci. Forum*, 2000, **347–349**(2), 303.
31. *Powder Diffraction File, Inorganic Volume*. File Card Nos. 5-0626 and 31-174. Joint Committee for Powder Diffraction Standards, Swarthmore, PA, 1990.
32. Uchino, K., Sadanaga, E. and Hirose, T., Dependence of the crystal structure on particle size in barium titanate. *J. Am. Ceram. Soc.*, 1989, **72**, 1555.
33. Arlt, G., Hennings, D. and de With, G., Dielectric properties of fine-grained barium titanate ceramics. *J. Appl. Phys.*, 1985, **58**, 1619.
34. Beck, H. P., Eiser, W. and Haberkorn, R., Pitfalls in the synthesis of nanoscaled perovskite type compounds. Part I: Influence of different sol-gel preparation methods and characterization of nanoscaled $BaTiO_3$. *J. Eur. Ceram. Soc.*, 2001, **21**, 687.
35. Yen, F.-S., Chang, C. T. and Chang, Y.-H., Characterization of barium titanyl oxalate tetrahydrate. *J. Am. Ceram. Soc.*, 1990, **73**, 3422.
36. Samara, G. A., Pressure and temperature dependence of the dielectric properties of the perovskites $BaTiO_3$ and $SrTiO_3$. *Phys. Rev.*, 1966, **151**, 378.
37. Li, X. and Shih, W.-H., Size effects in barium titanate particles and clusters. *J. Am. Ceram. Soc.*, 1997, **80**, 2844.
38. Kniepkamp, H. and Heywang, W., Über Depolarisationseffekte in polykristallinem $BaTiO_3$. *Z. Angew. Phys.*, 1954, **6**(9), 385.
39. Salje, E.K.H. Mesoscopic twin patterns in ferroelastic and co-elastic minerals. In: *Transformation Processes in Minerals. Reviews in Mineralogy & Geochemistry*, Vol. 39. Min. Soc. Am., Washington, DC, 2000, p. 65.
40. Salje, E. K. H. and Ishibashi, Y., Mesoscopic structures in ferroelastic crystals: needle twins and right-angled domains. *J. Phys.: Condens. Matter*, 1996, **8**, 1.
41. Stemmer, S., Streiffer, S. K., Ernst, F. and Rahle, M., Atomistic structure of 90-degree domain walls in ferroelastic $PbTiO_3$ thin films. *Phil. Mag.*, 1995, **A71**, 713.
42. Ustinov, A., Olikhovska, L., Niepce, J.-C. and Bernard, F., New possibilities for structural study of tetragonal crystals with twin microstructures using X-ray diffraction. In *Abstract Conference 'Accuracy in Powder Diffraction III'*. NIST, Gaithersburg, FL, 2001, poster 28.