

Characterization of Hydrothermal Barium Titanate

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(Received 23 March 1991; revised version received 7 May 1991; accepted 21 May 1991)

Abstract

Hydrothermally prepared powders of BaTiO_3 show a number of structural peculiarities which are closely connected with a considerable content of water, incorporated in the perovskite lattice. On annealing the powders to 500°C the water is gradually released and the normal structural properties of BaTiO_3 recur.

A defect chemical model has been derived for hydrothermal BaTiO_3 showing a loosely packed perovskite structure with large numbers of protons in the oxygen sublattice and vacancies in the sublattices of Ba and Ti.

Auf hydrothermalem Wege hergestellte BaTiO_3 -Pulver zeigen strukturelle Besonderheiten, die eng mit dem beträchtlichen Gehalt an Wasser im Perovskitgitter verknüpft sind. Beim Erhitzen auf 500°C geben die Pulver das Wasser schrittweise ab, wobei die strukturellen Eigenschaften des normalen BaTiO_3 wiederkehren.

Ein defektchemisches Modell wurde für hydrothermales BaTiO_3 aufgestellt, das eine locker gepackte Perovskitstruktur mit großen Mengen von Protonen im Sauerstoffgitter und Leerstellen in den Ba- und Ti-Plätzen zeigt.

Des poudres de BaTiO_3 préparées par voie hydrothermale ont un certain nombre de particularités structurales, très liées à la forte teneur en eau incorporée dans le réseau pérovskite. Par recuit de la poudre à 500°C , l'eau est progressivement éliminée et on retrouve les propriétés structurales normales de BaTiO_3 .

Un modèle sur les défauts chimiques en a été déduit pour ce titanate de baryum hydrothermal, décrivant une structure pérovskite faiblement 'remplie', avec un grand nombre de protons dans le sous-réseau de

l'oxygène et des lacunes dans les sous-réseaux de Ba et Ti.

1 Introduction

The common industrial routes of preparing BaTiO_3 for dielectric applications are calcination of mixtures of BaCO_3 and TiO_2 or thermal decomposition of Ba-titanyl-oxalate ($\text{BaTiO}[\text{C}_2\text{O}_4]_2 \cdot 4\text{H}_2\text{O}$) at temperatures in the range of 800 – 1100°C . Much lower temperatures of 150 – 200°C are needed for hydrothermal syntheses of BaTiO_3 . These syntheses usually start from mixed aqueous slurries of Ba and Ti hydroxide which can be completely transferred into fine-grained BaTiO_3 powder, using an autoclave at pressures of <5 MPa and strongly alkaline conditions ($\text{pH} > 12$).¹ Hydrothermal BaTiO_3 exhibits fine and fairly monodisperse particles of 0.2 – 0.4 μm crystallite size (Fig. 1), making these powders highly reactive and interesting for production of thin dielectric layers.

Hydrothermal BaTiO_3 shows a number of peculiarities which are not observed in powders produced by solid-state reaction at higher temperatures. X-ray diffraction (XRD) of such powders reveals a simple cubic perovskite structure which is normally observed only at temperatures above the ferroelectric Curie point at 130°C . Above that, hydrothermal BaTiO_3 contains considerable amounts of water which are gradually released upon heating the powders to temperatures of 100 – 500°C .

BaTiO_3 powders of similar crystallite size (0.2 – 0.4 μm) but produced by classical calcination show a tetragonally distorted perovskite structure. Only at very small crystallite sizes, $d < 0.15$ μm , these materials also become cubic at room temperature.²

The abnormal crystallographic features of hydro-

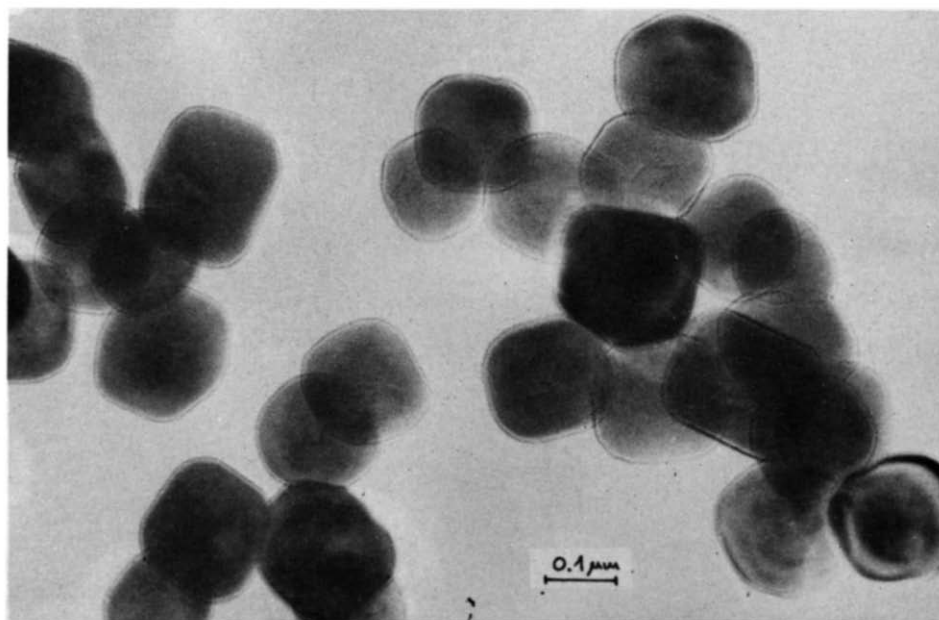


Fig. 1. Hydrothermally prepared barium titanate powder, TEM micrograph.

thermal BaTiO_3 are assumed to result from lattice defects, due to the water incorporated in the perovskite lattice. From acceptor-doped BaTiO_3 it is already known that appreciable amounts of OH^- can be taken up by the oxygen sublattice on firing these materials in moist reducing atmospheres ($\text{N}_2/\text{H}_2\text{-H}_2\text{O}$ mixtures).^{3,4} The hydroxyl defects heal out under emission of water by heating these materials at temperatures above 650°C ⁵ in dry atmospheres.

In this paper the correlations are studied between the content of chemisorbed water and the lattice structure of hydrothermal BaTiO_3 .

2 Experimental

Hydrothermal BaTiO_3 powders have been prepared from BaTi -acetate gel precursors, using a process described elsewhere.⁶ These powders were thermogravimetrically analysed (TGA, Netzsch STA 429) in the temperature range of $50\text{--}1100^\circ\text{C}$. Samples annealed in the temperature range $50\text{--}1000^\circ\text{C}$ were characterized by X-ray diffraction (XRD) and for evaluation of the specific surface area by BET (Surface Area Analyzer, Micromeritics, Norcross, USA). The density of annealed powders has been determined in a gas pycnometer, using He.

The presence of OH groups in BaTiO_3 can be detected by means of infrared (IR) spectroscopy. IR spectroscopical studies of hydrothermal BaTiO_3 have been performed in an IR spectrometer (Pye Unicam SP2000), using pills of powder pressed together with KBr. For distinguishing better the IR

absorptions of chemically bound water from those of adsorbed moisture, hydrothermal BaTiO_3 has been deuterated by heating the powders in D_2O for 16 h at 150°C in an autoclave and drying thereafter for 24 h at 80°C . In this way a large number of the OH groups could be exchanged for OD groups.

The diffusion length of the deuterons in BaTiO_3 at 150°C could be estimated, using the diffusion constant of deuterons in Mn-doped SrTiO_3 single crystals which had been determined by Waser³ for the exchange of protons by deuterons in the temperature range of $500\text{--}700^\circ\text{C}$. By extrapolating these values to 150°C (423 K) a diffusion constant $D_{(\text{D}/\text{H})} \approx 2 \times 10^{-13} \text{ cm}^2/\text{s}$ and a corresponding diffusion length of $x = \sqrt{D \cdot t} \approx 1.1 \mu\text{m}$ have been calculated for deuterons in BaTiO_3 at 150°C and a diffusion time of 16 h. The estimated diffusion length of $\approx 1.1 \mu\text{m}$ is much larger than the particle size of $0.2\text{--}0.3 \mu\text{m}$ of the hydrothermal BaTiO_3 , so that we can expect a total exchange of the protons by deuterons after heating the powders for 16 h at 150°C in heavy water.

3 Results

3.1 X-ray diffraction measurements (XRD)

Up to annealing temperatures of 200°C XRD revealed a cubic perovskite structure in hydrothermal BaTiO_3 powders. At higher temperatures the lattice parameters gradually reverted to tetragonal symmetry. The complete tetragonal distortion, $(c-a)/a \approx 1\%$, of the BaTiO_3 perovskite unit cell was obtained at temperatures above 600°C . Figure 2

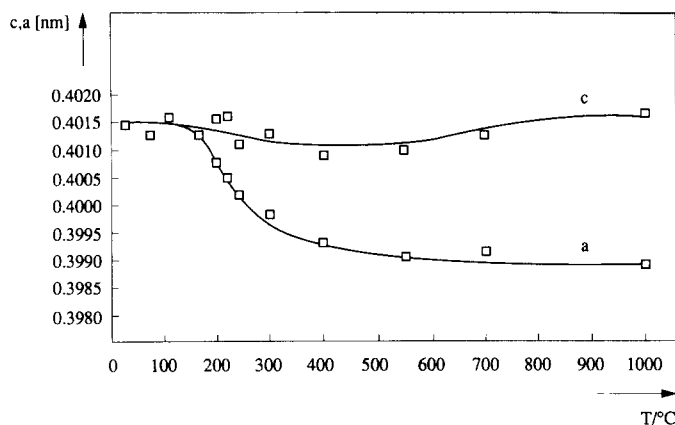


Fig. 2. Lattice parameters *c* and *a* of the tetragonal perovskite unit cell of hydrothermal BaTiO₃ as function of various annealing temperatures.

shows the lattice parameters of hydrothermal BaTiO₃ as function of the annealing temperature.

A special feature of hydrothermal BaTiO₃ is the enlargement of the unit cell volume. On annealing the BaTiO₃ in air in the range of 20–400°C the unit cell volume shrank by about 1.3% (Fig. 3). At least at 500°C the volume of the unit cell approached a value of $\approx 0.064(\text{nm})^3$, typical of 'normal' coarse-grained BaTiO₃. Both the enlargement of the unit cell volume and the cubic structure irreversibly disappear upon heating the powders in air to temperatures above 500°C.

3.2 Gas pycnometric measurements

Volume changes of annealed hydrothermal BaTiO₃ powders have been determined by means of gas pycnometry. For these measurements the BaTiO₃ powders were preheated for 16 h at various temperatures between 50 and 1100°C in a quartz vessel. In the temperature range of 50–700°C only a slight reduction of the powder volume was observed (Fig.

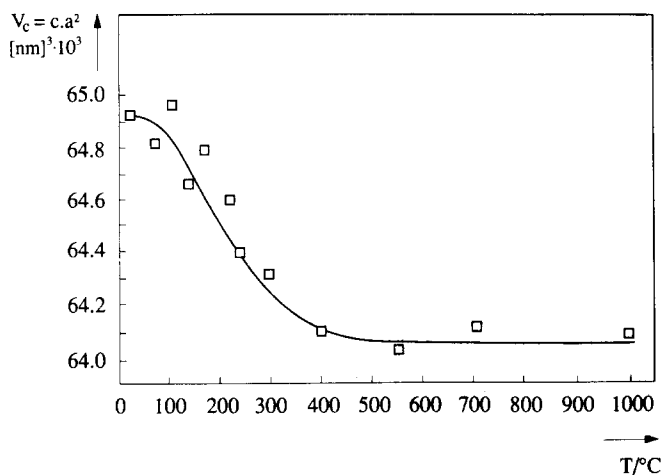


Fig. 3. Volume *V_c* of the perovskite unit cell of hydrothermal BaTiO₃, calculated from lattice parameters, plotted as function of various annealing temperatures.

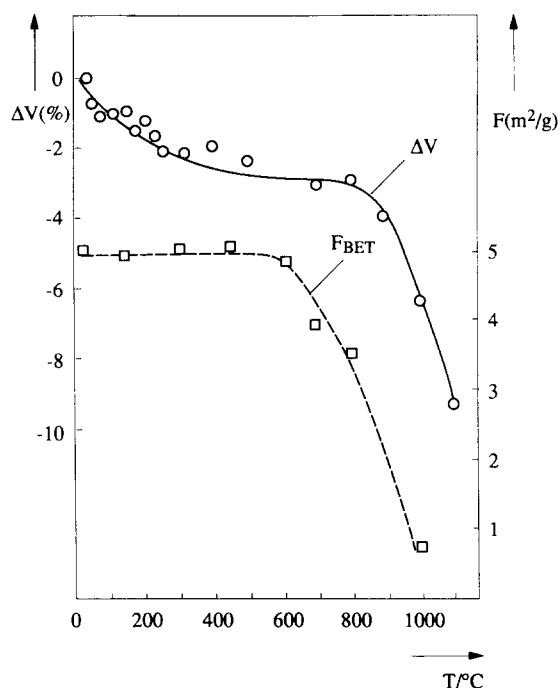


Fig. 4. Specific surface area *F* (m²/g), determined by BET, and volume changes ΔV (%), determined by gas pycnometric measurements, of hydrothermal BaTiO₃ powder, plotted as function of various annealing temperatures.

4). A more pronounced shrinkage of the powder volume occurred in the temperature region 800–1100°C. This larger shrinkage seems to be connected with the disappearance of inner porosity in the crystallites. Density changes of the powder have been calculated, with consideration of the small weight changes (H₂O losses). Up to 700°C the density of the BaTiO₃ remained practically constant, while a strong increase in density occurred at temperatures above 700°C (Fig. 5).

Under high magnification in TEM (Philips CM 12) hydrothermal BaTiO₃ often shows certain numbers of fissures and internal pores (Fig. 6) which obviously contribute to the specific surface area and the powder density.

3.3 Specific surface area

Up to annealing temperatures of 600°C the specific surface area of hydrothermal BaTiO₃ remained practically unchanged at about 5 m²/g. This value corresponds to an equivalent spherical diameter of $d_m \approx 0.2 \mu\text{m}$. The slight discrepancy in the average particle sizes, determined by different methods (sedimentation analysis, $d_{50} \approx 0.45 \mu\text{m}$; TEM, $d_{av} = 0.2\text{--}0.3 \mu\text{m}$), is probably due to morphological effects, e.g. particle agglomeration, and fissures. After heating the hydrothermal powders to 600°C a large reduction in the specific surface area was observed (Fig. 4).

The results of BET clearly show that particle

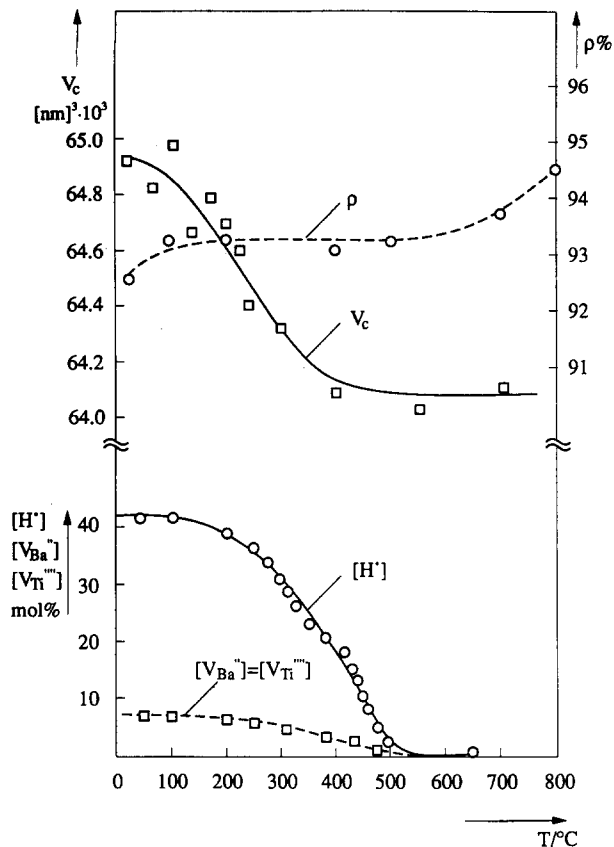


Fig. 5. Concentration of lattice defects $[\text{H}']$, $[\text{V}_{\text{Ba}}'']$ and $[\text{V}_{\text{Ti}}'''']$, unit cell volume V_c ($\text{nm})^3$ and relative density ρ (%), calculated from gas pycnometric measurements, of hydrothermal BaTiO_3 powder, plotted as functions of the annealing temperature.

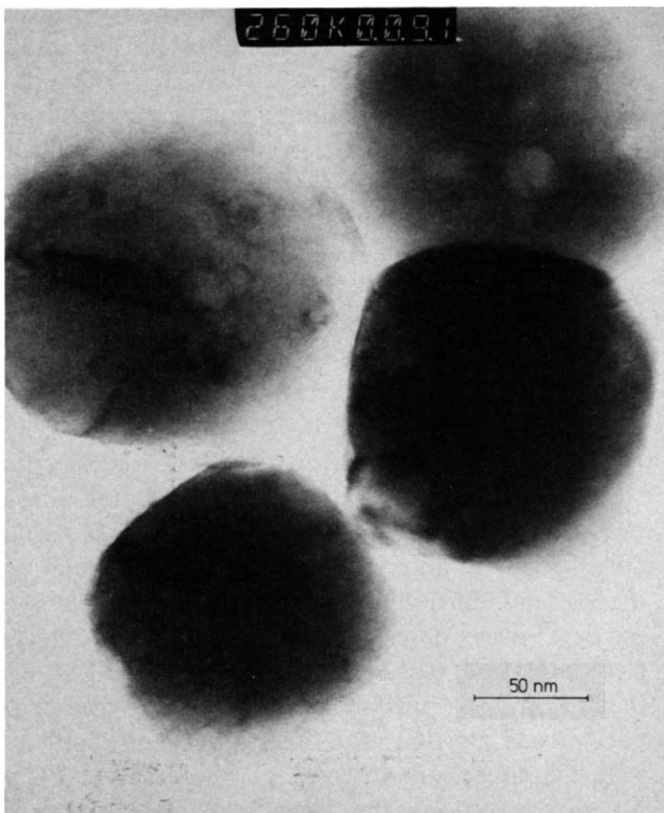


Fig. 6. TEM micrograph showing fissures and microporosity in a crystallite of hydrothermal BaTiO_3 .

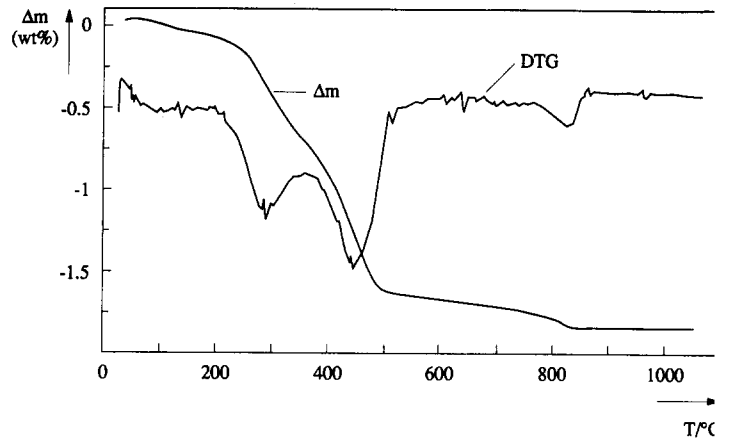


Fig. 7. Weight loss Δm (wt%) of hydrothermal BaTiO_3 in air, plotted as function of the annealing temperature, determined by TGA (heating rate $2^\circ\text{C}/\text{min}$).

growth and densification of hydrothermal BaTiO_3 are not significant at temperatures below 500°C . From this it can be concluded that the change from cubic to tetragonal structure, observed in the temperature range of $100\text{--}400^\circ\text{C}$, does not result from grain growth.

3.4 Thermogravimetry (TGA)

TGA experiments have been performed in air in the temperature range $50\text{--}1100^\circ\text{C}$ (Fig. 7). Between 100 and 500°C evaporation of *c.* 1.6 wt% water and at about $800^\circ\text{C} \approx 0.1$ wt% CO_2 were observed. Losses of CO_2 usually result from small BaCO_3 impurities, reacting with BaTiO_3 to form Ba_2TiO_4 at about 800°C .⁶ The rather high temperature at which the water is released from the BaTiO_3 strongly suggests chemisorption of OH groups in the perovskite lattice.

3.5 IR spectroscopy of hydrothermal BaTiO_3 powders

The deuterated and dried (80°C) hydrothermal BaTiO_3 was annealed for 6 h in air at 140 , 250 and 400°C to remove the water. A number of typical absorptions were found in the IR spectra of the annealed powders (Fig. 8) which could be attributed to the following functional groups:

OH: (absorbed water and moisture)⁷ at ≈ 3500 and $\approx 1640\text{ cm}^{-1}$;

OD: (absorbed D_2O)⁴ at $\approx 2600\text{ cm}^{-1}$;

CO_3 : (Ba-carbonate)⁷ at 1440 cm^{-1} ;

BaTiO_3 : (the 'fingerprints' of BaTiO_3)⁸ at 470 and 270 cm^{-1} .

As can be seen in Fig. 8, the OD adsorptions could be detected in all the deuterated samples, annealed up to 400°C . However, in the sample heated to 400°C the absorptions of OD became rather weak. The

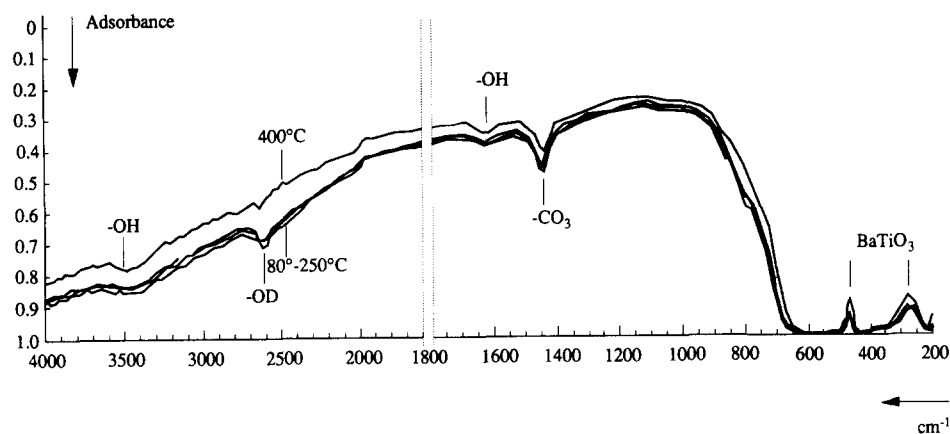


Fig. 8. IR spectra of deuterated hydrothermal BaTiO_3 , annealed at various temperatures in the range 50–400°C.

absorptions of OH, in contrast, remained equally strong in all samples annealed. From this it can be seen that the absorptions of chemisorbed OH in fact strongly interfere with those of moisture. From TGA experiments it is already known that BaCO_3 impurities are stable up to temperatures of 800°C in BaTiO_3 . For that reason the absorptions of CO_3 were found in all samples annealed up to 400°C.

4 Discussion

The investigation of hydrothermal BaTiO_3 has shown that these powders contain large amounts of chemically bound OH groups. In addition, a considerable enlargement of the unit cell volume and a suppression of the tetragonal distortion of the perovskite unit cell were observed.

Upon heating the powder gradually releases water in the temperature range of 50–450°C. The 'normal' crystallographic properties of coarse-grained BaTiO_3 gradually return at about 500°C. Below 500°C the changes in the specific surface area and the crystallite size are negligibly small (Fig. 4). Hence the restoration of the 'normal' crystallographic properties of BaTiO_3 at temperatures below 500°C cannot be a result of grain growth. There is rather a clear correlation between the amount of chemisorbed water and the abnormal crystallographic properties of hydrothermal BaTiO_3 .

If the water stemmed from amorphous second phases, e.g. unreacted $\text{TiO}(\text{OH})_2$, it should not markedly influence the crystallographic properties of the perovskite phase. Consequently the abnormal crystallographic properties of hydrothermal BaTiO_3 must therefore be discussed in terms of a defect chemical model, considering the OH groups, incorporated in the perovskite lattice.

Similar to the results of Waser,^{3–5} who detected protons in the oxygen lattice of BaTiO_3 which has

been previously annealed in moist atmospheres, we can assume protons forming hydroxide ions (OH^-) in hydrothermal BaTiO_3 as well. Protons on regular oxygen sites in the perovskite lattice must be considered as donors (H^+). In BaTiO_3 donors are usually compensated by acceptor-type metal vacancies, electrons or foreign acceptor ions.⁹ Because of the high purity and the light colour of the hydrothermal BaTiO_3 studied,⁷ compensation by either electrons or foreign acceptors can be excluded and only compensation of the proton donors by metal vacancies has to be taken into consideration.

The electroneutrality condition for the major defects in hydrothermal BaTiO_3 then can be formulated as

$$[\text{OH}^-] = 2[V_{\text{Ba}}^{''}] + 4[V_{\text{Ti}}^{''''}] \quad (1)$$

where, as in Kröger–Vink notation,¹⁰ V_{Ba} and V_{Ti} are respectively barium and titanium vacancies, and where the square brackets denote concentrations. Here it has been assumed that vacancy species are predominantly fully ionized, i.e. $V_{\text{Ba}}^{''}$ and $V_{\text{Ti}}^{''''}$.

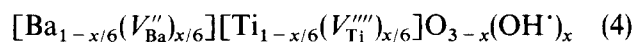
Precise analytical characterization of the Ba/Ti atomic ratio of the hydrothermal BaTiO_3 , using X-ray fluorescence (XRF), resulted in a nearly stoichiometric ratio of Ba/Ti $\approx 1:1.0015 (\pm 0.0015)$.⁷ For that reason, also equal numbers of Ba and Ti vacancies must be assumed for hydrothermal BaTiO_3 :

$$[V_{\text{Ba}}^{''}]/[V_{\text{Ti}}^{''''}] \approx 1 \quad \text{i.e.} \quad [V_{\text{Ba}}^{''}] \approx [V_{\text{Ti}}^{''''}] \quad (2)$$

Inserting eqn (2) into eqn (1) gives

$$[\text{OH}^-] = 6[V_{\text{Ba}}^{''}] \approx 6[V_{\text{Ti}}^{''''}] \quad (3)$$

From eqn (3) the formula of the defective hydrothermal BaTiO_3 , containing proton donors in the oxygen lattice and metal vacancies on Ba and Ti sites, has been derived:

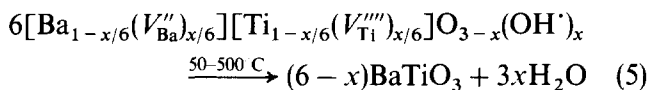


Upon heating the defective BaTiO_3 to 500°C water is



Fig. 9. TEM micrograph of sintered (1260°C in air) hydrothermal BaTiO₃ showing intragranular porosity.

evaporated and the lattice defects disappear, according to the reaction



From the maximum loss of water determined in the hydrothermal BaTiO₃, $\Delta m \approx 1.6 \text{ wt}\%$, the defect concentrations of $[\text{H}'] \approx 42 \text{ mol.}\%$ and $[\text{V}_{\text{Ba}}''] \approx [\text{V}_{\text{Ti}}'''] \approx 7 \text{ mol.}\%$ (referring to 1 mol. BaTiO₃) have been calculated.

The 'loosely packed' structure as well as the suppression of tetragonal distortion of the unit cell are both considered as the effect of the high proton concentration in the oxygen sublattice. A clear correlation has been found between the concentration of the lattice defects on the one hand and the volume enlargement of the perovskite unit cell on the other hand (Fig. 5).

Earlier studies on highly defective PbTiO₃¹¹ could not reveal a clear correlation between the concentration of metal vacancies and the volume of the unit cell. From this it can be derived that the 'loosely packed' perovskite structure of hydrothermal BaTiO₃ is most probably a joint effect of the large number of defects in the three sublattices of oxygen, barium and titanium, which reduce the Coulomb attractive forces between the ions.

It is interesting to note that the density of the hydrothermal BaTiO₃ powder is hardly affected by

annealing procedures at temperatures below 700°C (Fig. 5). The rather low relative density of $\approx 93\%$ at 700°C is most probably an effect of intragranular porosity in the crystallites of hydrothermal BaTiO₃. The internal pores partly disappear at temperatures above 800°C. However, in ceramics sintered from hydrothermal BaTiO₃, often large numbers of small intragranular pores are found by using TEM (Fig. 9). The intragranular pores are probably formed by concentration of migrating vacancies and water inside of pores.

Acknowledgements

We wish to express our gratitude to Dr R. Waser for stimulating discussions, Mr G. Rosenstein for producing the transmission electron micrographs, Mrs U. Gontermann-Gehl for performing the BET and gas pycnometric measurements, and H. D. Bausen for evaluating the XRD measurements.

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