

Effect of calcination on characteristics, surface texture and sinterability of chemically prepared barium titanate

N. M. GHONEIM, S. HANAFI*, TH. SALEM*

National Research Centre, and *Ain-Shams University, Kasr-El-Zaafaran, Abbasiya Cairo, Egypt

Highly pure and finely divided barium titanate powders have been obtained by the pyrolysis of barium titanyl oxalate. The effect of time and temperature of calcination on the degree of crystallinity, fineness, and surface texture of the powders obtained have been demonstrated. The densification properties of the sintered bodies are discussed in relation to the characteristics of the calcined materials.

1. Introduction

Since the discovery of the unique ferroelectric properties of barium titanate ceramics during the Second World War, intensive practical and theoretical studies have been made to improve its properties and widen its technological applications. Several studies have dealt with the effect of purity and powder fineness of the starting materials on the physical and electrical properties of BaTiO₃ ceramics [1-4]. Traditional solid-state techniques of preparation introduce detrimental impurities, during processing, which has a negative effect on these properties [5, 6]. Furthermore, the lack of homogeneity or uniformity, within the materials used, presents another problem when using such traditional methods. The development of the wet chemical routes of preparation has offered reasonable high purity, high degree of compositional homogeneity and a small uniform particle size barium titanate starting powders [7-9]. Although these characteristics have been studied by some researchers [9-11], the surface texture of such powders and its relation to the subsequent ceramic properties has not yet received the attention it deserves. The relatively large surface areas of barium titanate powders, obtained by chemical methods, mean that highly sinter-active materials are expected on firing and therefore adequate surface characterization and its effect on the subsequent sintering process is needed.

In the present work, barium titanate powders, obtained by pyrolysis of barium titanyl oxalate under different calcination conditions, have been characterized for their composition, degree of crystallinity and particle sizes. The surface areas and pore structure of the different powders have been investigated. The effect of surface texture and reactivity of the powders on the sintering behaviour of the barium titanate compacts has been discussed.

2. Experimental details

2.1. General procedures

All chemicals used were reagent grade. The BaTiO₃ used in the present study was obtained by the pyrolysis

of BaTiO-(C₂O₄)₂ · 4H₂O. This barium titanyl oxalate tetrahydrate was prepared by the procedure devised by Clabaugh *et al.* [7] in which a cooled mixed solution of equimolar amounts of barium chloride and titanium tetrachloride was allowed to drip slowly into a hot (80 to 85°C) vigorously stirred solution of oxalic acid. Experiments showed that a slight excess of BaCl₂ (0.01 mol %) and a greater excess of oxalic acid (0.1 mol %) result in better barium to titanium stoichiometric ratio in the precipitate. The precipitate was hot filtered to avoid the possibility of precipitation of different compositions on cooling. The precipitate was washed with chilled distilled water several times and finally with acetone. The batch size was maintained at 0.5 mol barium titanyl oxalate.

The air-dried precipitates were thermally analysed using thermogravimetry (TG) and differential thermogravimetry (DTG) to determine the effects of heating using a Du Pont 990 thermal analyser. A heating rate of 10° min⁻¹ was used, and samples weighing 0.20 g were placed in platinum crucibles throughout the runs. The thermal behaviour was studied in a stagnant air atmosphere. X-ray diffractometer tracings of the heated samples were obtained using a "Siemens" diffractometer (D 500) with CuK α radiation and a nickel filter and a scanning speed of 2° min⁻¹. The thermal analysis data indicate the temperature at which theoretical weight loss is reached and this was arbitrarily selected as the minimum calcination temperature. The stoichiometric ratio was checked by wet chemical analysis and batches which gave BaO/TiO₂ ratio deviating from unity were not used in this study. The samples were also analysed for their purity using an emission spectrographic technique.

The medium infrared absorption spectra were determined for the calcined powders using a Beckman Spectrometer IR 4250. In-line transmission was measured on thin sections (1.0 mm thick) using a glass standard. A 2 mg sample of each powder was dispersed in 200 mg anhydrous spectrographic grade KBr powder and pressed into discs for infrared studies.

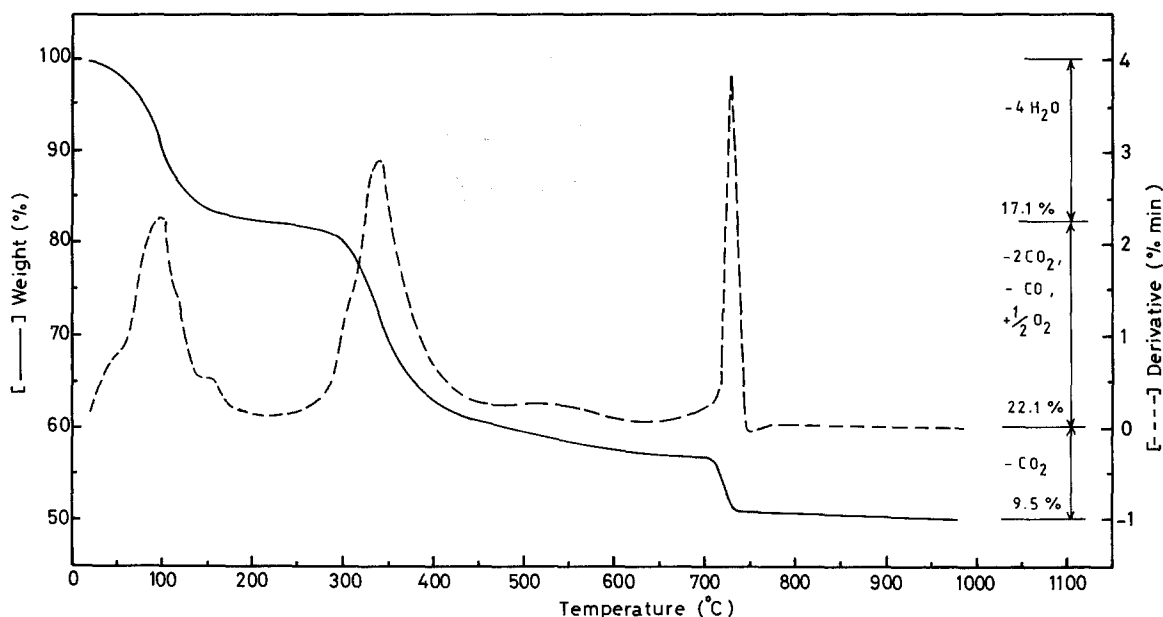


Figure 1 TGA and DTG curves for barium titanyl oxalate in air.

Particle size and shape were studied using an E 10 Zeiss transmission electron microscope (TEM). Copper grids of 0.2 cm diameter coated with carbon film were used as the sample support. Each sample was dispersed in acetone using an ultrasonic bath for 15 min. The powders were not tumbled before dispersion.

2.2. Measurement of surface characteristics

The surface textures were investigated by the adsorption of nitrogen gas at liquid nitrogen temperature using a BET volumetric apparatus of the conventional type. Before each adsorption run the powder was out-gassed at 200°C for 3 h.

2.3. Fabrication and sintering

The calcined powders were uniaxially cold-pressed into discs 12 mm diameter and ~3 mm thick using a stainless steel die. A two-step fabrication pressure of 5000 p.s.i. (34.45 Nmm^{-2}) maintained in all formings. The compacts were sintered in air at 1250 to 1450°C for 1 h in a muffle furnace with SiC heating elements. A firing rate of 200 to 250°C h⁻¹ was employed in all firings.

The densification properties, namely linear shrinkage and bulk density, were measured for the sintered bodies. Bulk densities were determined geometrically and checked by pycnometry in CCl₄ and only results giving close similarity are considered.

3. Results and discussion

The results of TG and DTG analyses are presented in Fig. 1, from which it is clear that the four water molecules are evolved in an unresolved three-step loss that extends from 30 to ~200°C. A broad DTG curve follows and extends from ~250 to 460°C, peaking at 340°C, and is accompanied by an isothermal-like weight loss. The amount of loss is not equivalent to the evolution of 2 CO₂ or 4 CO as proposed in other works [10–12].

Gallagher and Thomson [13], using effluent gas and thermogravimetric analyses, considered that BaTiO(C₂O₄)₂ ions decompose to BaCO₃ and TiO₂,

after acquiring oxygen from the ambient, with the evolution of 1 CO and 2 CO₂ molecules. The presence of a DT exothermic reaction in this temperature range [11] substantiates this proposal because the release of CO shows as an exothermic peak in the presence of oxygen. Furthermore, the XRD pattern of the material heated to 550°C shows weak broadened lines corresponding to BaCO₃. The measured loss in weight (22.1%) also agrees with the calculated loss based on this mechanism. The isothermal-like loss is followed by a gradual one until 700°C where a sudden final drop in weight is observed peaking at 730°C. This loss in weight is equivalent to one molecule of CO₂. This thermal behaviour is similar to that obtained by Gallagher and Thomson [13] with only a slight shift in temperatures of peaking. This shift is attributed to the difference in the rates of heating.

It is supposed that the reaction between the finely divided, intimately mixed, and highly reactive BaCO₃ and TiO₂, formed between 300 and 400°C, occurs later than the early formation of BaTiO₃, than if the conventional materials were mixed and calcined.

From the results of TGA it is clear that the reaction is complete by 730°C and the calcination temperatures are chosen above it. Therefore, the powders were calcined at temperatures between 750 and 1200°C for different soaking times. XRD patterns (Fig. 2) show that the increase in both calcination temperature and time is accompanied by increase in the intensity of diffraction lines denoting increased crystallite size. All diffraction lines agree well with the ASTM values for tetragonal BaTiO₃.

Emission spectrographic analysis showed a high degree of purity for the prepared titanates (>99.95%). Reproducible results have been obtained for the different batches prepared.

The medium infrared characteristic absorption frequencies of the stoichiometric highly pure BaTiO₃ powders calcined at 750 and 850°C for 1 h, and at 1000°C for 12 h, are shown in Fig. 3. The figure illustrates the position and intensities of the medium IR absorption spectra of the tetragonal BaTiO₃ pow-

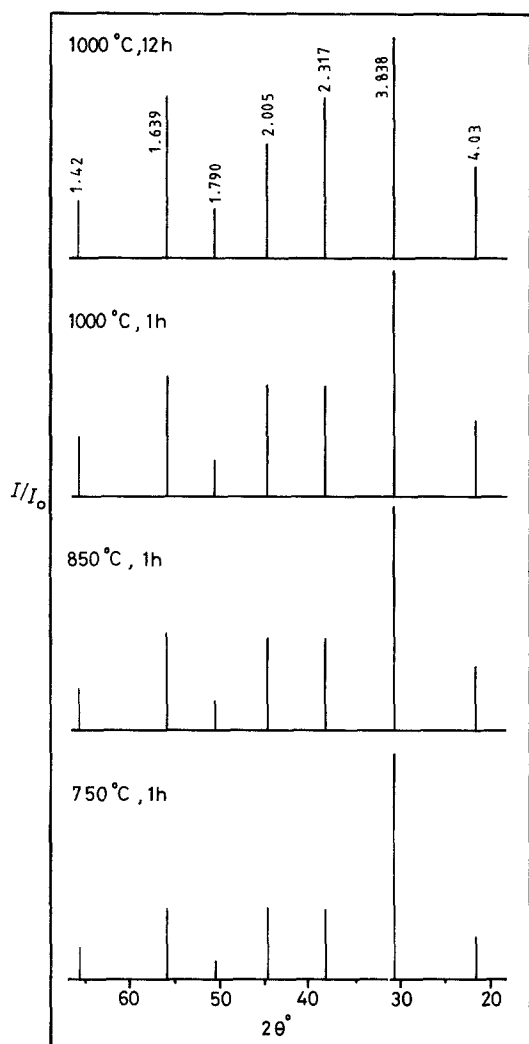


Figure 2 XRD lines of barium titanate calcined at different temperatures.

der. The bands at 530 to 570 cm^{-1} and 360 to 400 cm^{-1} agree well with results reported by Last [14] and by Spitzer *et al.* [15] for BaTiO_3 in polycrystalline powder form. The bands exhibit a slightly more defined shape as the temperature is raised, probably due to the increase in crystallinity.

The selected photomicrographs, for the particle size and shape of the powders calcined at different temperatures and time durations, are shown in Fig. 4. In Figs 4a and b, fine sub-rounded particles with the majority of the particles in the submicrometre range are observed for the powder calcined at 750°C (1 h). A limited tendency towards agglomeration is also observed. From the electron micrographs the mean particle size was found to range between 0.1 and $0.2\ \mu\text{m}$. This range nearly matches the values obtained by Gallagher and Schrey in their work on oxalate-derived titanate powders [11]. A high reactivity is expected from this powder on subsequent sintering reactions. As the temperature and time of calcination are increased, both the mean particle size and agglomeration tendency are noticeably enhanced and the number of particles in the submicrometre range decreased; Figs 4c and d show photomicrographs of powders calcined at 850 and 1000°C , respectively. The opaque and angular nature of agglomerates of these powders is evident from the photomicrographs, par-

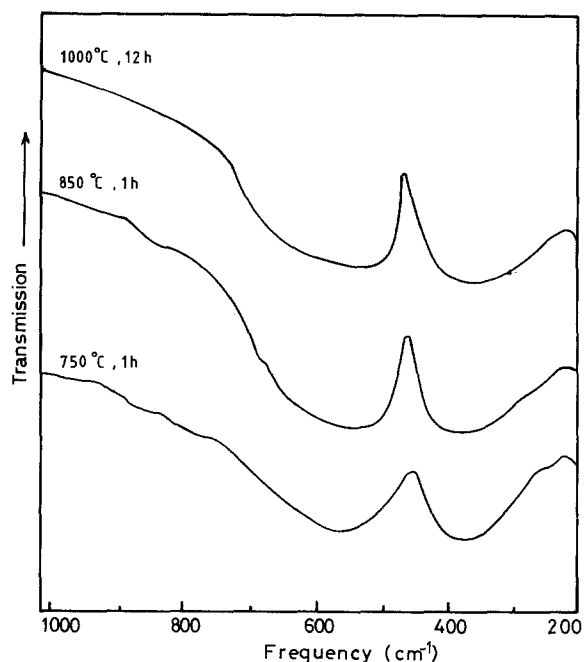


Figure 3 Medium infrared spectra of BaTiO_3 powders calcined under different conditions.

ticularly for powder calcined at 1000°C (12 h). Its wide range of particle sizes is expected to offer good packing conditions on fabrication.

Complete adsorption-desorption isotherms of nitrogen gas at liquid nitrogen temperature (-195.8°C) were measured volumetrically for BaTiO_3 powders, calcined at different temperatures, and are shown in Fig. 5. All isotherms show the common characteristics of nearly type II of Brunauer's classification. They are characterized by being irreversible with closed hysteresis loops indicating the presence of mesopores as a part of the total pore system. The hysteresis loop diminishes continuously with increasing temperature of calcination, denoting a decrease in the mesopore fraction of the total pore system.

Specific surface areas were derived by the Brunauer-Emmett-Teller (BET) method in the conventional range of relative vapour pressure, adopting a value of 1.62 nm^2 for the molecular area of nitrogen. The total pore volumes are calculated from the amount of nitrogen adsorbed at the saturation vapour pressure of the adsorbate and expressed in millilitres of liquid nitrogen per gram adsorbent (V_p ; ml g^{-1}). The hydraulic radius (nm) of the total pore system is

$$\bar{r}_h = \frac{V_p}{S_{\text{BET}}} \times 10^3$$

Some of the surface characteristics derived from the nitrogen adsorption data are summarized in Table I. A specific surface area of $70.2\text{ m}^2\text{ g}^{-1}$ has been obtained for BaTiO_3 powder calcined at 750°C (1 h); this represents a fairly high surface area with a relatively low total pore volume. Both surface area and total pore volume decrease gradually as the temperature of calcination increased up to 1000°C . At 1100 and 1200°C the nitrogen adsorption proceeds mainly via the diffusion mechanism; therefore, high values of S_{BET} and S_t (surface area as obtained from V_t-t plot as explained in the next paragraph) are observed despite the fact that the particle sizes increased noticeably at

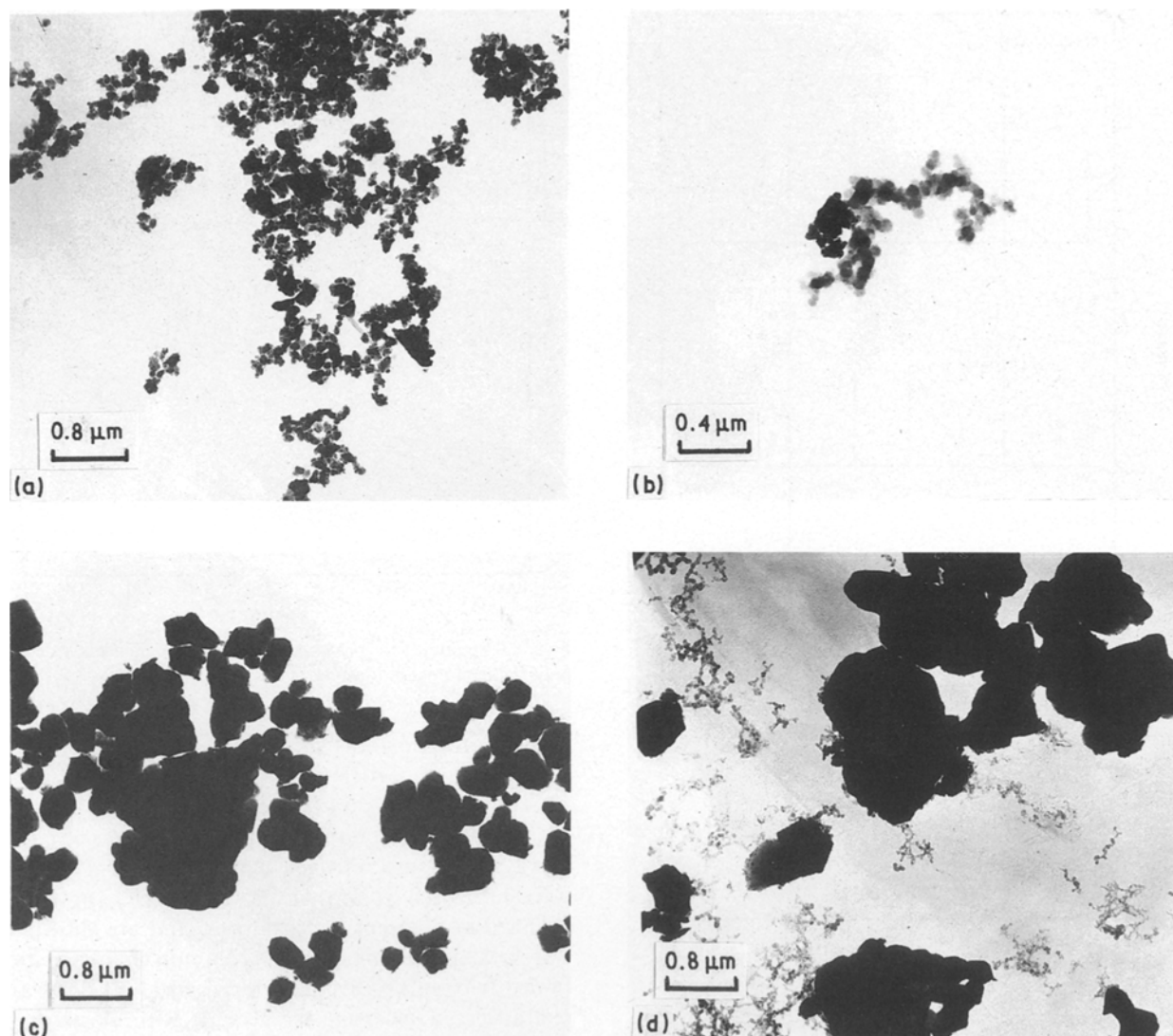


Figure 4 Transmission electron micrographs of calcined BaTiO₃ powders.

these high calcination temperatures; meanwhile, the total pore volume decreases. The mean hydraulic radius, \bar{r}_h , also shows a slight decrease as temperature is raised to 1000°C; this behaviour is mainly associated with enhanced accessibility of nitrogen molecules to a major part of the total pore system due to the increased crystallinity of the powders, as indicated in the X-ray reflections of Fig. 2. Because all powders are calcined, though at different temperatures, a low heat of interaction between adsorbate molecules and their surfaces is obtained. The more or less constancy of BET-c (constant calculated from the adsorption-desorption cycles of nitrogen. It is a measure of the heat (energy) of interaction between the adsorbed nitrogen molecules and the measured powder surface) over the

investigated calcination temperature reflects this behaviour.

The modifications of surface texture by calcination can also be observed by carrying out a pore structure analysis using the *t*-method of Lippens *et al.* [16, 17] to differentiate between the existence of micropores and mesopores in the samples. The plots of the volume of liquid adsorbate absorbed, expressed in millilitres per gram adsorbent (V_t ; ml g⁻¹), against the statistical multilayer thickness of the adsorbed layer (*t*; nm) are shown in Fig. 6. The values of *t* reported here are those obtained by Mikhail *et al.* [18] for the low-heat adsorbent-adsorbate interactions. A slight deviation from the straight lines is noticed at relatively high *t*-values for powders calcined at 750, 850 and 1000°C, denoting almost non-porous materials. For 1100 to 1200°C calcined powders, an upward deviation appears in the plot at $t \approx 0.56$ nm which turns to a downward deviation at $t \approx 0.12$ nm. This suggests the existence of mesopores with limited sizes together with some micropores.

TABLE I Surface characteristics of BaTiO₃ powders calcined at different temperatures for 1 h

Calcination temperature (°C)	S_{BET} (m ² g ⁻¹)	S_t (m ² g ⁻¹)	BET-c constant	V_p (ml g ⁻¹)	\bar{r}_h (nm)
750	70.2	68.0	5	0.1778	2.5
850	52.6	53.5	5	0.1030	2.1
1000	44.4	42.5	4	0.0913	2.0
1100	59.5	58.0	3	0.0756	1.3
1200	60.5	58.0	3	0.0750	1.3

From the above mentioned results, it is obvious that BaTiO₃ powder calcined at 750°C exhibits the highest S_{BET} value (70.2 m² g⁻¹) while calcination at 1000°C offers the lowest specific surface area (44.4 m² g⁻¹). It is a matter of interest to investigate the effect of

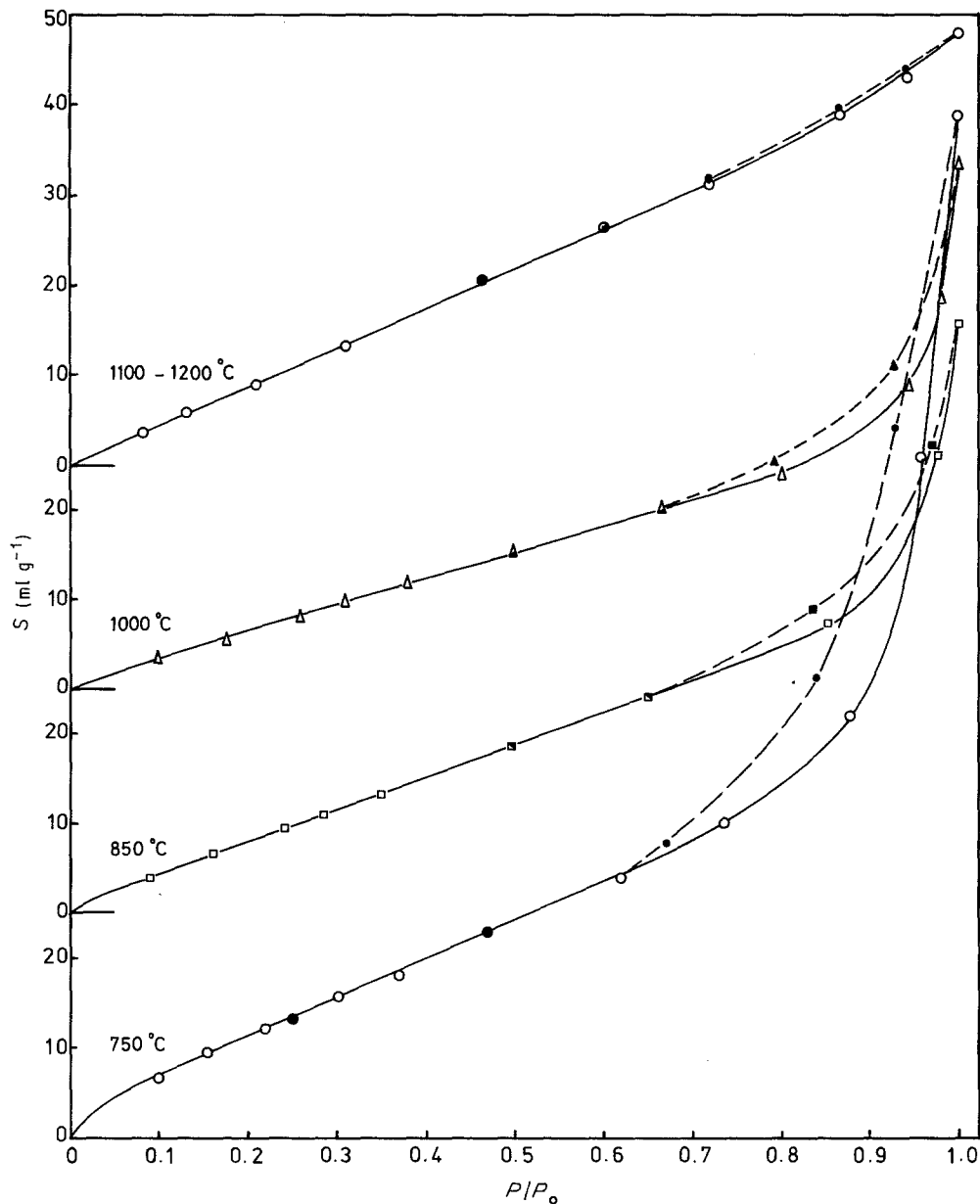


Figure 5 Adsorption (○)–desorption (●) isotherms of nitrogen for BaTiO₃ powders calcined at different temperatures for 1 h.

isothermal heatings at these temperatures on their surface textures. Adsorption–desorption isotherms of nitrogen were obtained for these two powders and the surface characteristics are given in Tables II and III. From Table II it can be seen that increasing time of soaking from 1 to 18 h at 750°C decreases the S_{BET} of the material from 70.2 to 52.3 m² g⁻¹. It is generally accepted [19] amongst researchers that fine reactive powders tend to reduce their solid–vapour interphase areas on heating. In other words, they tend to reduce their total surface free energy to reach a lower energy stable state; as a consequence fine particles grow larger on sintering. Therefore, the observed decrease in sur-

face area by isothermal heating at 750°C can be attributed to the growth of crystallites forming the powder. The stability in surface characteristics proceeds in two stages. In the first stage, stabilization of a particular size of crystallites takes place and is terminated before 6 h soaking time is reached. The downward deviations from the straight line at high t -values for 1 and 3 h soakings, and the upward deviation for 6 h soaking in the V_t - t plots of Fig. 7 substantiate this criterion very well. At 12 h soaking, the crystallites grow larger with the development of large crystals surrounded by minute amorphous-like crystallites; this effect leads to some sort of compensation between the capillary condensation in mesopores and micropore filling as is

TABLE II Surface characteristics of BaTiO₃ powders calcined at 750°C for various periods of time

Soaking time (h)	S_{BET} (m ² g ⁻¹)	S_t (m ² g ⁻¹)	BET-c constant	V_p (ml g ⁻¹)	\bar{r}_h (nm)
1	70.2	68.0	5	0.1778	2.5
3	60.9	64.0	6	0.1310	2.2
6	61.5	64.0	5	0.1264	2.2
12	52.9	51.0	4	0.0967	1.8
18	52.3	52.0	4	0.0930	1.8

TABLE III Surface characteristics of BaTiO₃ powders calcined at 1000°C for various periods of time

Soaking time (h)	S_{BET} (m ² g ⁻¹)	S_t (m ² g ⁻¹)	BET-c constant	V_p (ml g ⁻¹)	\bar{r}_h (nm)
1	44.4	42.5	4	0.0913	2.1
3	42.8	39.0	4	0.0803	1.9
6	35.9	33.0	4	0.0601	1.7
12	34.0	30.0	4	0.0538	1.6

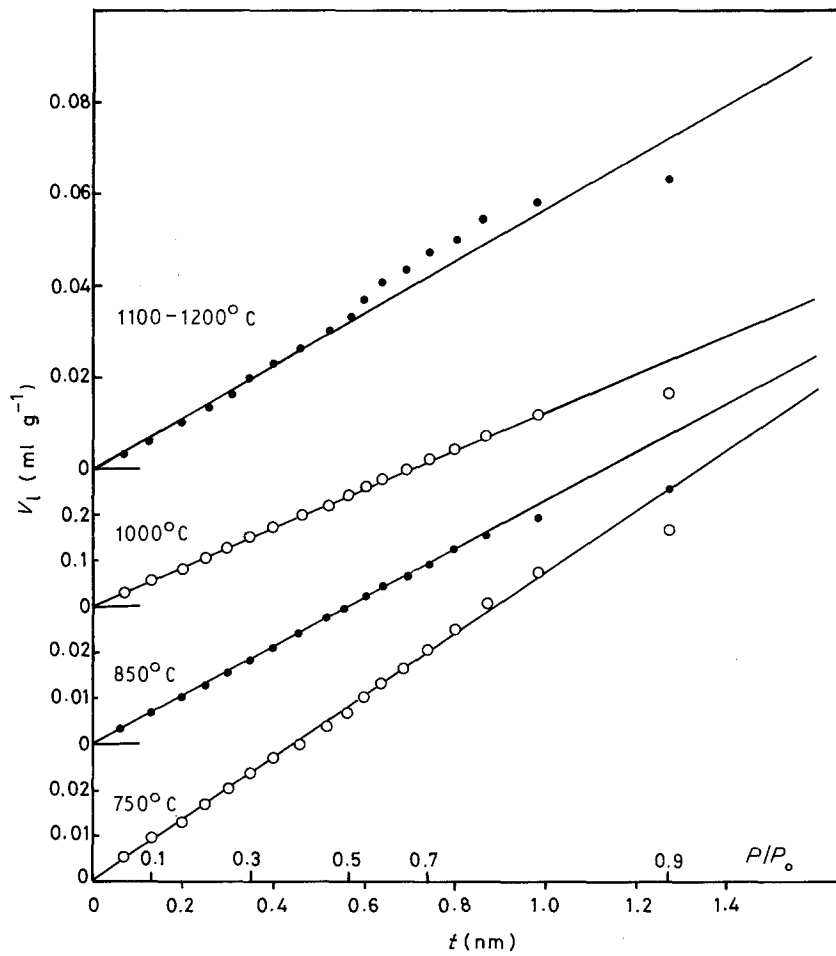


Figure 6 V_1-t plots from nitrogen adsorption data for BaTiO_3 calcined at different temperatures for 1 h.

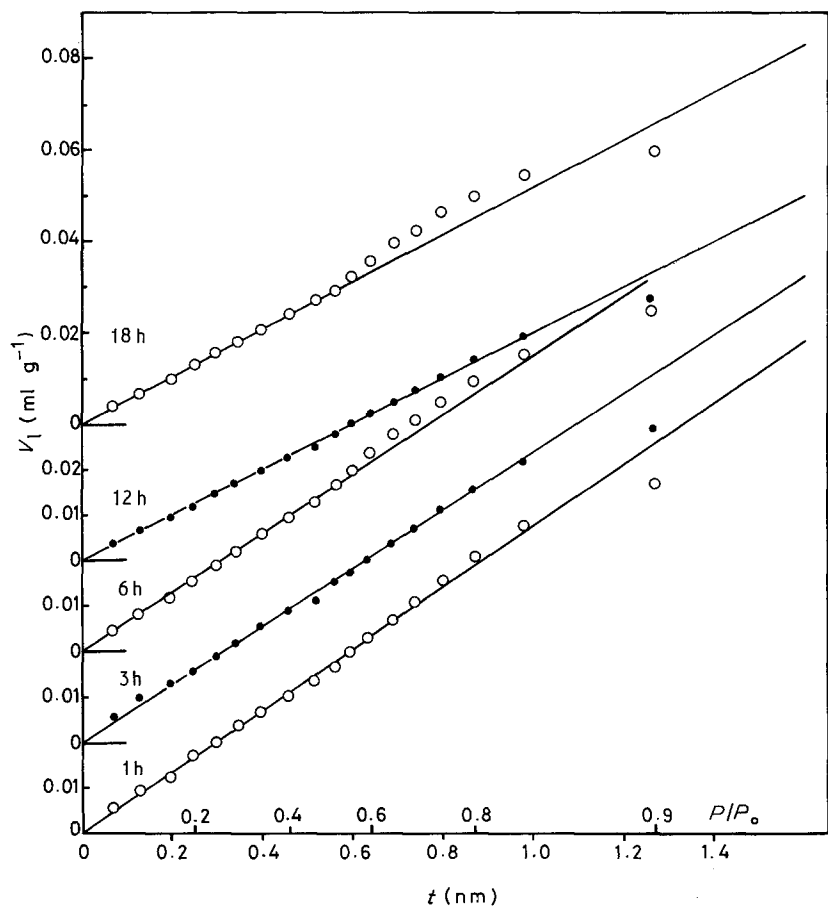


Figure 7 V_1-t plots from nitrogen adsorption data for BaTiO_3 calcined at 750°C for various periods of time.

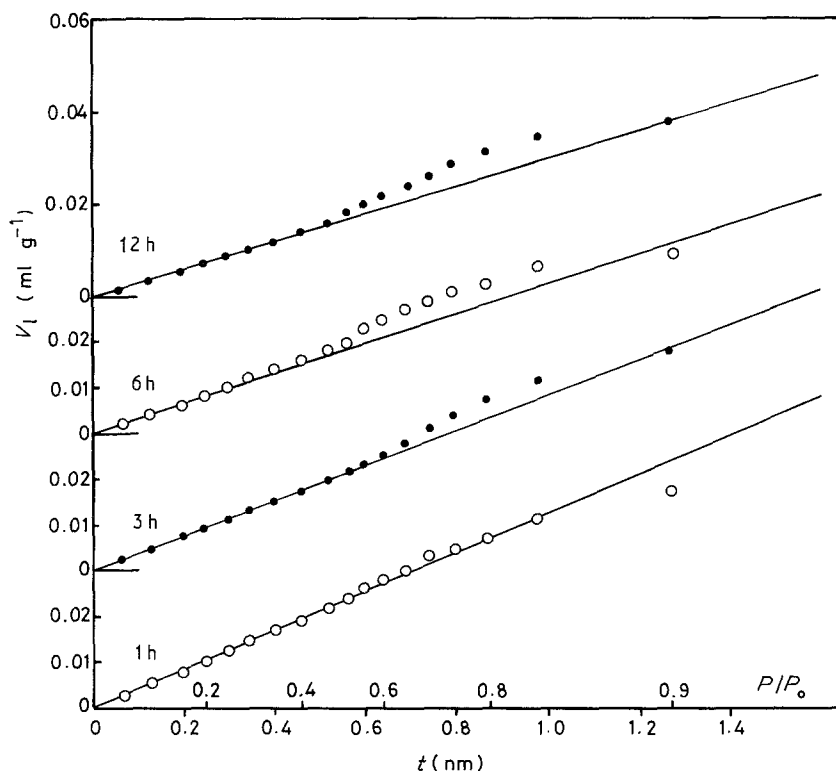


Figure 8 V_1-t plots from nitrogen adsorption data for BaTiO_3 calcined at 1000°C for various periods of time.

reflected in the linear V_1-t plots obtained close to the saturation pressure. Finally, at 18 h soaking, the adsorption is mainly via a diffusion mechanism; the minute crystallites diffuse to the surface of the larger ones leading to crystal growth as mentioned above. The total pore volume, V_p , and hydraulic radius, \bar{r}_h , decrease with calcination time parallel to the step-wise decrease observed for S_{BET} .

For barium titanate powder calcined at 1000°C (Fig. 8), longer soaking times are accompanied by increase in the fraction of mesopores in the total pore system. Such a result denotes an opening of the pore system to nitrogen molecules. This trend is reflected from the continuous upward deviation from the initial straight line in the V_1-t plot as the soaking time increases. However, the effect of crystal growth with increasing time of calcination at 1000°C predominates and leads finally to a net decrease in the total surface area and total pore volume.

From Tables II and III, the BET-c constants lie within the low range of heat of interaction between the adsorbed molecules and the surface of the investigated materials. The continuous slight decrease in the radii of the pore system reflects the decrease in the inter-granular spaces. The development of agglomeration as temperature and time of calcination increase could explain the high accessibility of nitrogen molecules towards the measured surface because the intra- rather than inter-agglomerate porosity develops to a greater extent at high calcination conditions of such highly pure oxide material powders [10, 20].

The low heat of adsorption of nitrogen on these solids (as indicated by the low values of the BET-c constants) proves that nitrogen has a non-specific interaction with the solid surfaces, and the weak physical (Van der Waal) forces of adsorption are predominant.

The densification properties of the sintered com-

pacts, fabricated from the powders calcined at 750 and 850°C for 1 h and at 1000°C (12 h), were measured and the fired specimens are referred to as BT-I, BT-II, and BT-III, respectively. Bulk density (% theoretical density) and per cent linear shrinkage of the fired specimens are plotted against firing temperature in Fig. 9. Long firing times are observed for all the BT specimens between 1250 and 1450°C , indicating the high degree of purity and Ba/Ti ratio close to unity exhibited by these materials [21]. BT-I and BT-II specimens show a sharp increase in their densities from 1250 to 1300°C , followed by a gradual decrease on firing up to 1450°C . Density values of 97.7% and 96.7% theoretical are obtained at 1300°C for BT-I and BT-II, respectively. On the other hand, BT-III specimens displayed the lowest density values over the whole firing range with a smooth maximum of 95.2% theoretical at 1350°C . The presence of a maximum in densification, followed by a gradual decrease on further firing, was also found by other investigators on processing chemically prepared barium titanates [4, 22, 23]. However, the values obtained here are higher, probably due to the difference in characteristics of the processed materials. Furthermore, the maxima achieved in densities are at temperatures 80 to 100°C lower than the temperature required for sintering the commercial material. The linear shrinkages show their high values at temperatures of maximum densification for each BT specimen group; virtually no further increase in shrinkage is observed on further firing.

The differences between the highly pure barium titanates investigated including particle size and shape, tendency towards agglomeration and degree of reactivity, seem to exert a significant influence on the subsequent ceramic properties. The high surface area and noticeably fine individual particulates with uniform size distribution of the BaTiO_3 powder calcined at 750°C for 1 h offered a highly sinterable material on firing of

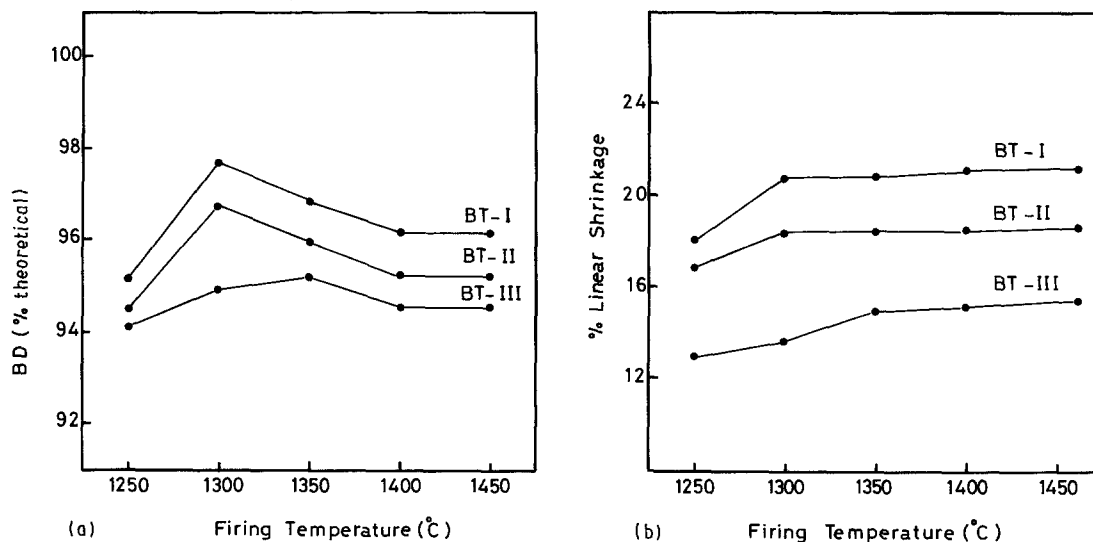


Figure 9 (a) Bulk density (% theoretical), and (b) per cent linear shrinkage of the BaTiO₃ fired bodies at different firing temperatures (1 h).

its compacts; a dense body with a shrinkage of about 21% is achieved at as low as 1300°C. The decrease in densification on further firing could be attributed to the inevitable discontinuous grain growth that usually takes place on sintering such reactive oxides [4, 19, 23, 24]. This situation could also apply to BT-II specimens prepared from the still reactive powder calcined at 850°C for 1 h. On the other hand, the coarse particles with wide distribution of sizes and lower surface area attained by the powder calcined at 1000°C for 12 h, makes the material less susceptible to discontinuous grain growth on firing. Partial densification of the material occurred during calcination, offering pre-reacted powder which on compaction and sintering exhibited the least shrinkage and density values among the investigated BT specimens. Furthermore, intra-agglomerate voids could develop between the hard agglomerates and surrounding matrix during early stages of sintering [25]. This type of pore may not close, leading to a halt in densification before theoretical density is reached.

It can be concluded from the results that calcination conditions are significant in influencing the powder characteristics and surface texture of chemically prepared BaTiO₃. Lower calcination temperatures and shorter soaking periods give the desired results; a material with significantly fine and uniform particle size and high surface area, hence lower temperatures, is required to bring about maturity to the ceramic body on firing.

Acknowledgement

The authors thank Dr S. A. Abo El-Enein, Professor of Physical Chemistry, Ain-Shams University, for valuable discussions.

References

1. R. EUBANK, F. T. ROGERS, L. E. SHILBERG Jr and S. SKILNIK, *J. Amer. Ceram. Soc.* **35** (1952) 16.

2. E. P. HYATT and H. R. LAIRD, *Amer. Ceram. Soc. Bull.* **45** (1966) 541.
3. R. J. GRAF, *Ceram. Age*, **58** (6) (1951) 16.
4. E. P. HYATT, S. A. LONG and R. E. ROSE, *Amer. Ceram. Soc. Bull.* **46** (1967) 732.
5. K. NELSON and R. L. COOK, *J. Amer. Ceram. Soc.* **38** (1959) 499.
6. M. DÉRI, *Periodica Polytechn. Chem. Engng* **4** (1960) 307.
7. W. S. CLABAUGH, E. M. SWIGGARD and R. GILCHRIST, *J. Res. Nat. Bur. Stand.* **56** (1956) 289.
8. B. J. MULDER, *Amer. Ceram. Soc. Bull.* **49** (1970) 990.
9. K. S. MAZDIYASNI, R. T. DOLLOFF and J. S. SMITH, *J. Amer. Ceram. Soc.* **52** (1969) 523.
10. K. KISS, J. MAGDER, M. S. VUKASOVICH and R. J. LOCKHART, *ibid.* **49** (1966) 291.
11. P. K. GALLAGHER and F. SCHREY, *ibid.* **46** (1963) 567.
12. B. V. STRIZHKOV, A. V. LAPITSKII and L. G. VLASOV, *Zh. Priklad. Khim.* **33** (1960) 2009.
13. P. K. GALLAGHER and J. THOMSON Jr, *J. Amer. Ceram. Soc.* **48** (1965) 644.
14. J. T. LAST, *Phys. Rev.* **105** (1957) 1740.
15. W. G. SPITZER, R. C. MILLER, D. A. KLEINMAN and L. E. HOWARTH, *Phys. Rev.* **126** (1962) 1710.
16. B. C. LIPPENS, B. G. LINSEN and J. H. DE BOER, *J. Catal.* **3** (1964) 32.
17. J. H. DE BOER, B. G. LINSEN and TH. J. OSINGA, *ibid.* **4** (1965) 643.
18. R. SH. MIKHAIL, N. M. GUINDY and S. HANAFI, *Egypt. J. Chem. Sp. Issue Tourky* (1973) 53.
19. W. D. KINGERY, H. K. BROWN and D. R. UHLMANN, "Introduction to Ceramics" (Wiley, New York, London, Sidney, Toronto, 1975).
20. M. A. C. G. VAN DE GRAAF, K. KEIZER A. BURGGRAAF, *Sci. Ceram.* **10** (1980) 83.
21. E. J. BRAYER and D. BERLINCOURT, Office of Naval Research Centre, USA Technical Report no. 12 (1955).
22. E. C. HENRY, A. V. ILLYN and W. TANTRAPORN, US General Electric Report no. 17, March 31 1962.
23. J. V. BIGGERS and W. A. SCHULZE, *Bull. Amer. Ceram. Soc.* **51** (1972) 620.
24. N. M. GHONEIM, PhD thesis, Technical University of Veszprém, Hungarian Academy of Sciences, June 1976.
25. W. H. RHODES, *J. Amer. Ceram. Soc.* **64** (1981) 19.

Received 13 June

accepted 12 September 1989