

Uniaxial Hot-Pressing of Fine-particle, Pure Barium Titanate without Die*

J. Liebertz

Institut für Kristallographie der Universität zu Köln,
Zülpicher Str. 49, D 5000 Köln 1, FRG

SUMMARY

The hot-forging of fine-particle, pure barium titanate was studied in the temperature range 1050–1200°C at pressures of between 10 and 100 MPa. To enable pressure sintering to be carried out without the use of a die, cold-pressed green compacts of relatively small thickness were used. Test samples of a very high density ($D_{rel} > 0.96$) were obtained at 1150 and 1200°C and at medium pressures within about 15 min. There was little grain growth. The kinetics of the hot-pressing of $BaTiO_3$ are reported and discussed.

1 INTRODUCTION

Uniaxial hot-pressing enables high-density ceramic bodies to be produced without additional sintering aids, so that the desired purity of the finished product is not impaired. By applying higher pressures it is possible to reduce the sintering temperature appreciably and to shorten the sintering time considerably. A further advantage compared with conventional sintering at zero pressure is the small degree of grain growth.

Hot-pressing of barium titanate has been studied by several investigators^{1–6} using graphite, alumina or zirconia dies. With graphite, partial chemical reduction of the specimens has to be taken into account. Preliminary tests with alumina dies yielded only unsatisfactory results. For these reasons, the present work aimed at hot-forging without dies. The kinetics of densification were studied, and suitable process conditions for

* The experimental part of this study was carried out at the Aachen Research Laboratory of Philips GmbH.

producing non-porous dielectric ceramics were determined. Hot-forging could possibly be employed for the production of multilayer capacitors, without delamination of dielectric ceramic layers and metal electrodes.

2 HOT PRESSING EXPERIMENTS

2.1 Apparatus

The compressive force of the apparatus is applied via a controllable oil hydraulic system, attaining a maximum value of 250 kN. The pressing pistons (60 mm diameter) in contact with the sample consist of sintered alumina cylinders which, to reduce heat conduction, are butted to alumina tubes. A drilled hole in the upper piston enables a thermocouple to be mounted close to the test sample. The test sample together with the pistons are enclosed by a close-fitting ceramic protective tube so that, if necessary, a desired atmosphere can be maintained.

An electric resistance furnace, which can generate temperatures up to a maximum of 1240°C at the test sample, surrounds the protective tube. The heating-up time to 1200°C is approximately 2 h. A control system ensures a temperature stability of $\pm 3^\circ\text{C}$.

A dilatometer with an accuracy of 0.001 mm, which provides a measured value every 10 s, is used for monitoring the reduction in the thickness of the test sample during hot-forging.

2.2 Preliminary tests

In hot-pressing it is customary to use dies. The technique described in this paper was also tried with alumina dies, but without success: during hot-pressing the test sample permanently stuck. Covering the dies with a platinum film or smearing with a ZrO_2 suspension failed to solve this problem. The usefulness of alumina dies⁵ could not be confirmed.

For this reason, hot-forging without dies, i.e. without lateral support of the sample, was attempted. This method proved feasible if predensified green compacts were used. The adhesion of the sintered compacts to polished alumina pistons could generally be avoided by means of a thin layer of ZrO_2 powder suspended in an organic binder. With a sufficiently high diameter to thickness ratio for the cylindrical test samples (tablets), the lateral strain was surprisingly low; for example, only about 4% with a final ratio of 10:1.

2.3 Starting material

BaTiO_3 'HPB' (TAM Ceramics Inc., Niagara, USA) was used. The powder is characterised by high purity (total impurity less than 300 ppm) and good

stoichiometry ($\text{TiO}_2:\text{BaO} = 1.006$). The average particle size was about $0.9 \mu\text{m}$. According to STEM tests, the average diameter of the crystallites was about $0.4 \mu\text{m}$, which corresponds to the specific surface of $3.59 \text{ m}^2 \text{ g}^{-1}$ obtained by BET.

2.4 Production of the green compacts

Two major considerations determined the dimensions of the test samples. For actual pressures of some 10 MPa the diameter had to be chosen such that the hydraulic system used was in a reasonable working range. A diameter of 40 mm for the green compacts was therefore appropriate. In order to keep the lateral strain down to a negligible level, a thickness of just under 2 mm had to be used.

The starting powder was mixed with a 5% or 10% polyvinyl alcohol solution and granulated. For each experiment approximately 8 g of granules were compressed into a tablet in a steel die (40 mm diameter) using a hand-operated press worked at approximately 200 MPa. The relative density of each tablet was about 0.55. To burn out the binder, the tablets were heated for some hours up to 600°C . The test samples prepared in this way were then subjected to hot-forging.

2.5 Experiments and results

A slight contact pressure of approximately 0.5 MPa was applied during the heating-up period in order to fix the position of the test sample and thermocouple in the furnace. Once the desired sample temperature had been attained, the working pressure was applied within 2 min, and the thickness shrinkage of the test sample was subsequently measured with the dilatometer.

Thermal equilibrium had to be ensured in order to avoid any errors in the linear shrinkage due to the thermal expansion of the apparatus. A change in working temperature of 1°C corresponded to a virtual elongation of the test sample by $\pm 1\text{--}2 \mu\text{m}$.

The densification curves, i.e. relative density versus time, were calculated from the dilatometer recordings, the final density and the final thickness of the test sample. The lateral strain of 0.5–1.5% was not taken into account, especially since it could not be observed as a function of time. The curves must be calculated back from the final data because the state of the samples when starting dilatometry differed greatly from the green state. Because of the method used it was not possible to register the initial phase of densification during the heating-up period and also during the application of pressure. This is shown in the density curves (Figs 1–4) by the marked

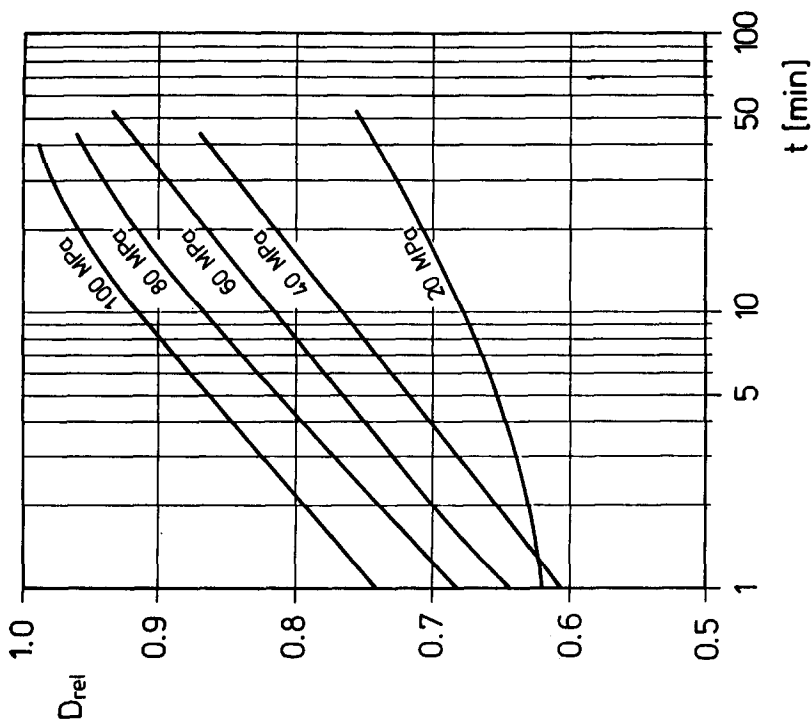


Fig. 2. Density at 1100°C as a function of time and pressure.

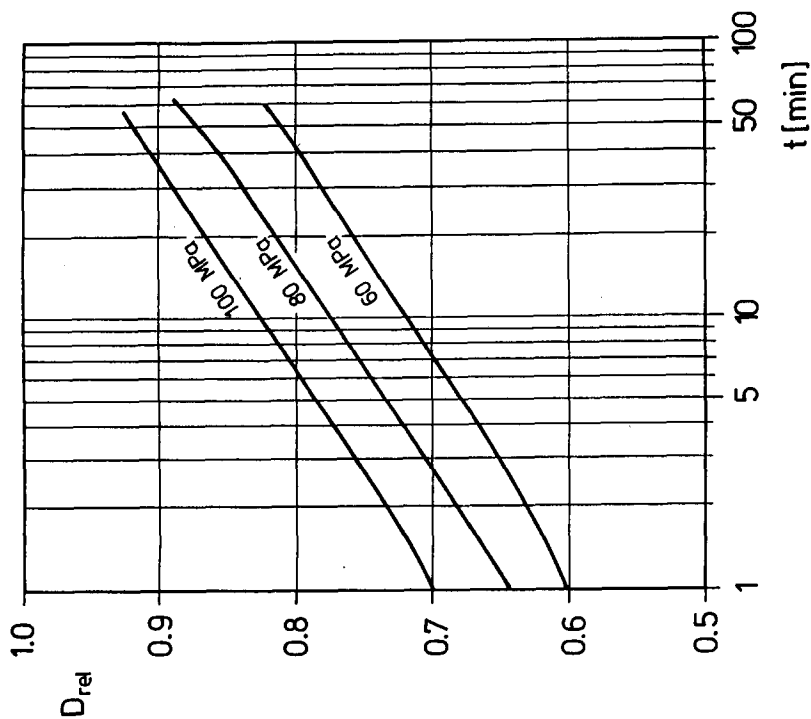


Fig. 1. Density at 1050°C as a function of time and pressure.

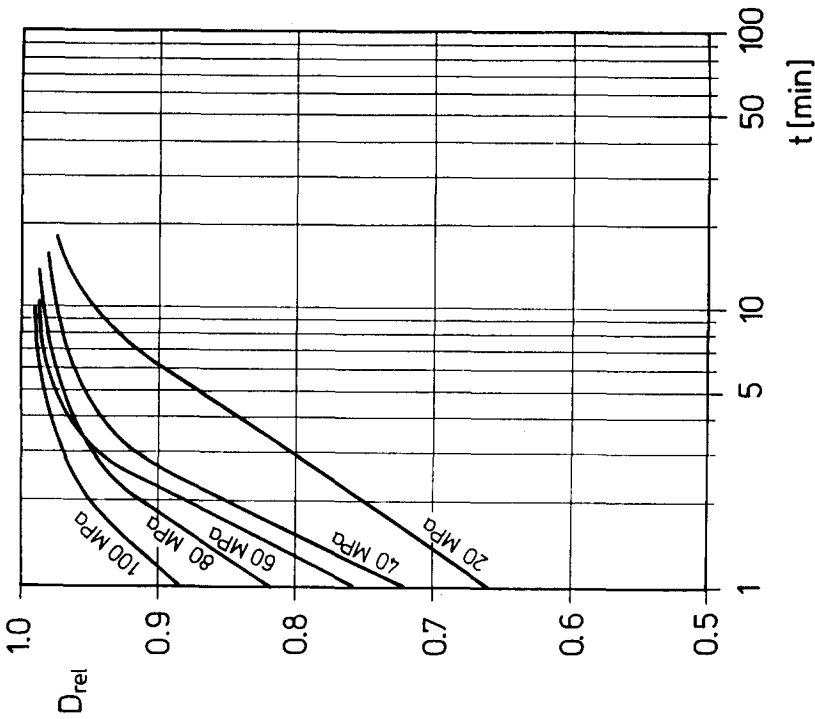


Fig. 4. Density at 1200°C as a function of time and pressure.

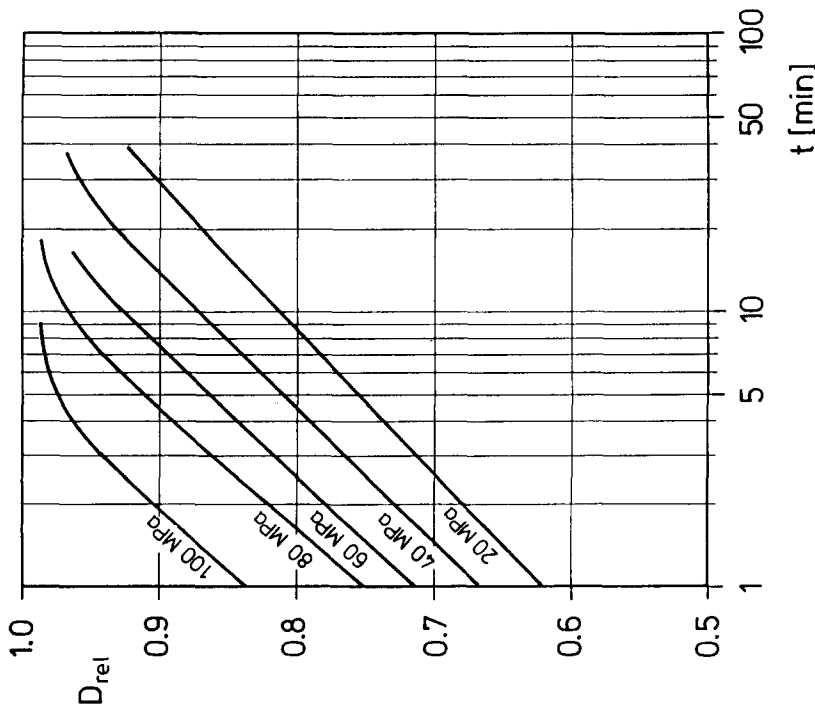


Fig. 3. Density at 1150°C as a function of time and pressure.

variations in initial density. The total error of the relative densities of the sintering curves is estimated to be $\pm 1\%$ for high values (closed porosity) and $\pm 5\%$ for low values (open porosity).

The hot-forging experiments covered temperatures of between 1050 and 1200°C and pressures of between 10 and 100 MPa. The experiments were terminated when there was no longer any worthwhile densification, at the latest after 60 min. The individual conditions are shown in summarised form in a P-T diagram (Fig. 5).

As the diagrams (Fig. 5, and in detail Figs 1-4) show, the required high relative density of at least 0.96 can be achieved within an hour or less in the temperature range 1100-1200°C. With increasing temperature, the appropriate pressure can be lowered. However, excessively high pressures were destructive, regularly causing the test sample to break up. The range of favourable conditions is indicated in Fig. 5 by the two curves. From this we can derive, as standard parameters, temperatures of around 1150-1200°C and medium pressures of between 30 and 60 MPa, which tallies with the observations of Crayton and Price.⁷

The densification curves (Figs 1-4) were obtained as described above. For convenience, the pressure was varied in 20 MPa steps. Where a curve was

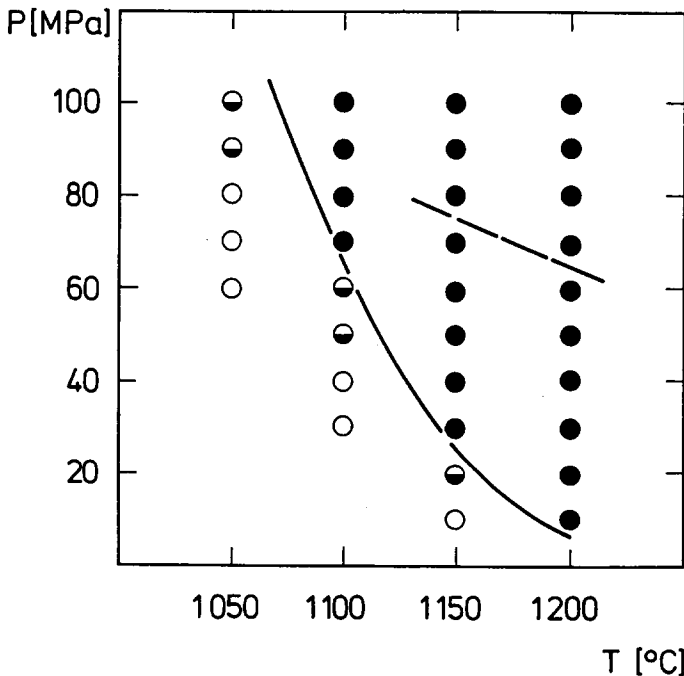


Fig. 5. P-T Diagram of the hot-forging experiments. ○ $D_{rel} < 0.92$; ● $D_{rel} > 0.96$. Above the dashed line the samples were found to be broken. Time of applied pressure between 15 and 60 min.

based on two tests, the average was taken. The densification curves show the effect of temperature and pressure on sintering behaviour. An increase of both parameters results in a higher final density or a shorter sintering time for a fixed density. Given favourable P - T conditions approximately 15 min is sufficient to ensure a high final density.

Owing to the higher pressures applied in the present experiments, dense samples ($D_{rel} > 0.96$) were obtained at considerably lower temperatures than those used by Mostaghaci and Brook.¹

3 TESTS ON THE CERAMIC SAMPLES

Microscopic examinations of the test samples showed that porosity was always highest in the peripheral zone, which is understandable because of the radial pressure gradient. Occasionally, the pore distribution in the denser

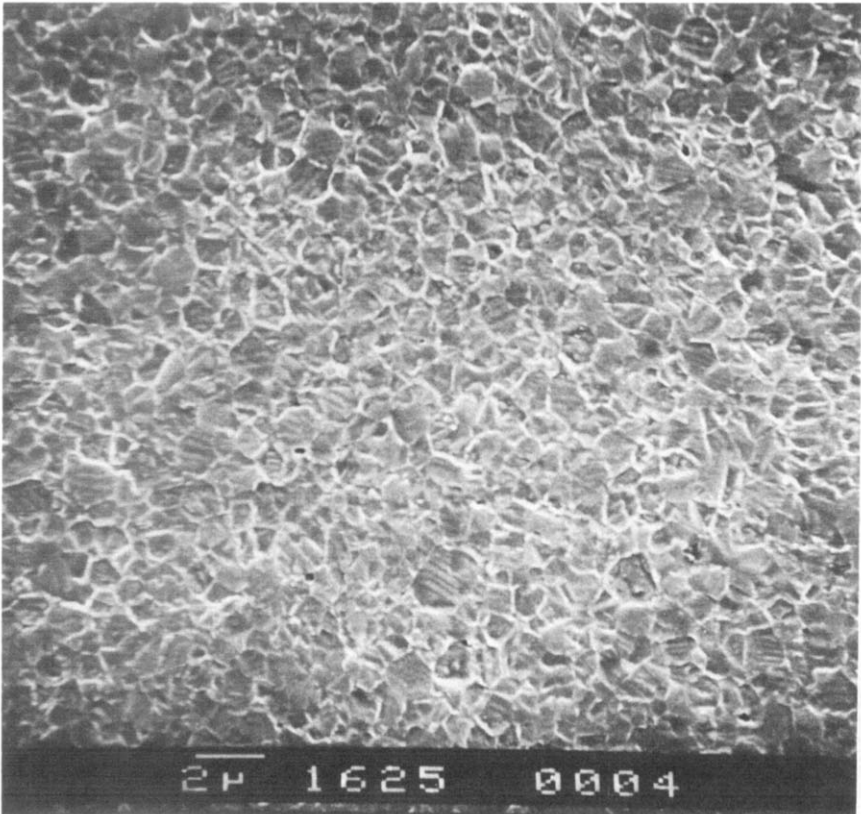


Fig. 6. SEM micrograph of polished and etched BaTiO_3 specimen, obtained after 10 min at 1200°C and 60 MPa.

core area was less homogeneous than expected. This corresponded with fluctuations in the measured density of test samples if cut into several parts. The cause of this may be that there was already a certain degree of heterogeneity in the green compact. Completely dense areas could be recognised with the naked eye by their glassy appearance.

The light-microscopic resolution was not sufficient for a microstructural examination. However, examination with the scanning electron microscope (Fig. 6) showed a very uniform structure with grain diameters of between 0.5 and 1.5 μm (starting diameter approximately 0.4 μm). Grain growth was thus not very pronounced.

X-ray examination of the surface of the test samples by a diffractometer did not indicate any preferential orientation of the grains.

4 DISCUSSION

The logarithmic time scale in Figs 1–4 illustrates the kinetics of hot-pressing. The curves show, with the exception of that for 1100°C and 20 MPa, a constant slope for relative densities <0.95; above a relative density of 0.95 the curves flatten. The linear part of the curves is described using the time law given by Vieira and Brook⁸

$$D_{\text{rel}} = D'_{\text{rel}} + C \times \ln(t)$$

in which D'_{rel} is the density for $t = 1$, and C is a constant. Of course this approach must fail close to $D_{\text{rel}} = 1$. Obviously, the slopes (C) increase with increasing temperature and in a first approximation are independent of the pressure (Figs 1–4). The values of D'_{rel} , which account for the initial stage of the pressure sintering, increase both with temperature and with pressure.

The densification rate is usually represented by the empirical relationship

$$\dot{D}_{\text{rel}} = K \times P^n \exp(-Q/RT)$$

in which K is a material constant containing amongst others the diffusion coefficients, while P = pressure, n = pressure exponent and Q = activation energy. As far as the constant K is concerned, a detailed discussion of the mechanisms of hot-pressing only makes sense if one has sufficient knowledge of the material constants involved. There is no difficulty, however, in obtaining the pressure exponents and the activation energy from the experimental data.

In order to estimate the activation energy, the logarithm of the densification rate was plotted versus the reciprocal absolute temperature for $D_{\text{rel}} = 0.85$, $P = 80$ MPa. As can be seen from Fig. 7, the activation energy (Q) amounts to 486 kJ mol⁻¹ which is in good agreement with the value of 506 kJ mol⁻¹ previously observed.¹

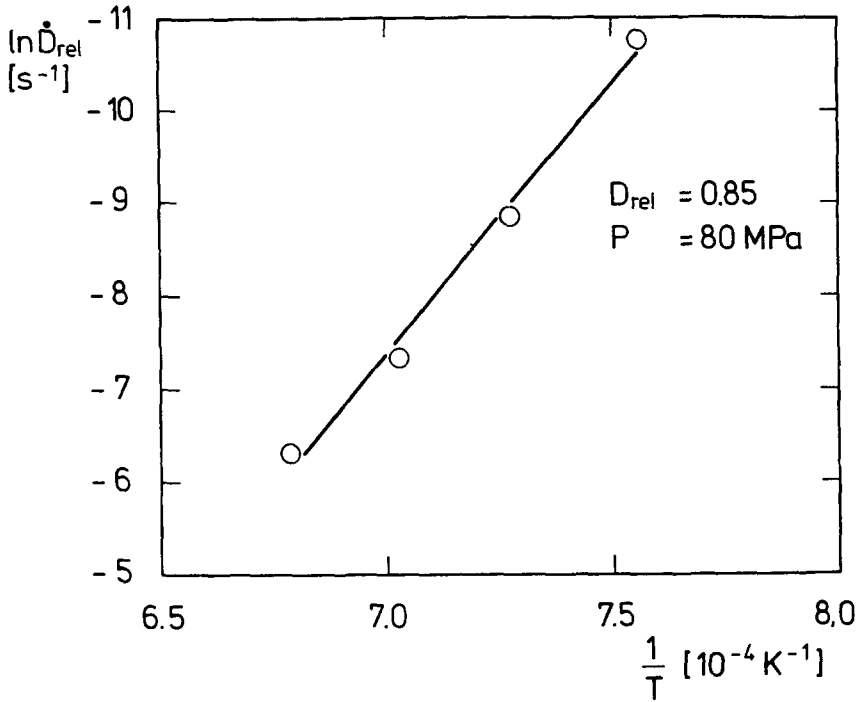


Fig. 7. Densification rate as a function of reciprocal temperature.

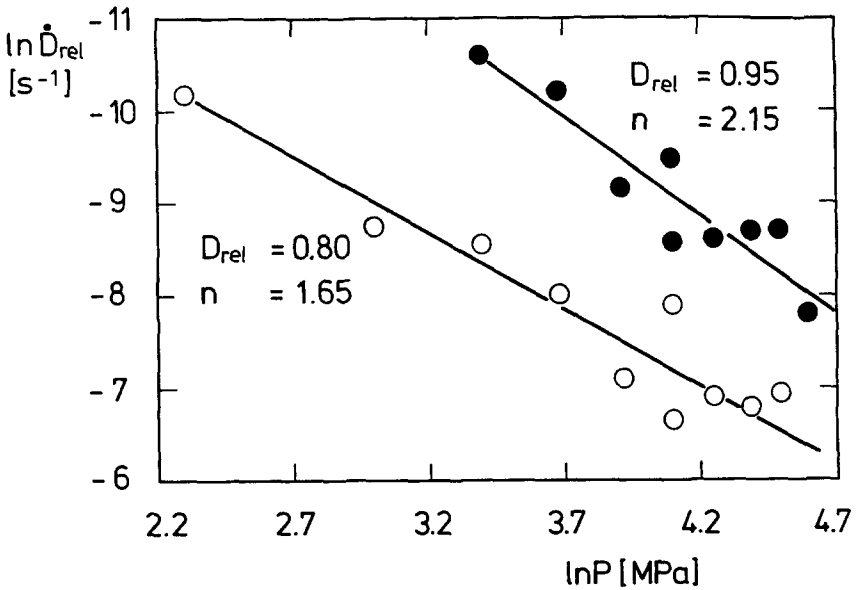


Fig. 8. Densification rate at 1150°C as a function of pressure.

If at a fixed temperature, $\ln D_{\text{rel}}$ is plotted versus $\ln P$, the pressure exponent (n) can be derived from the slope. This is depicted in Fig. 8 for 1150°C and the relative densities 0.80 and 0.95. The pressure exponent (n) is equal to 1.65 for $D_{\text{rel}} = 0.80$ and equal to 2.15 for $D_{\text{rel}} = 0.95$, whereas Mostaghaci and Brook¹ found that n was approximately equal to 1 for $D_{\text{rel}} = 0.8$. From hot-pressing experiments as well as creep tests at high temperatures and pressures,⁹⁻¹¹ exponents between 1.5 and 2.5 are commonly reported for oxides. The stress exponent $n = 1$ applies both to Nabarro-Herring creep,^{12,13} which is based on volume diffusion of vacancies, and Coble creep¹⁴⁻¹⁶ which is due to surface diffusion. A further explanation for $n = 1$ is the presence of a liquid boundary phase considered by Mostaghaci and Brook¹ which, however, can be excluded here because of the high purity and good stoichiometry of the starting material. On the other hand, $n = 3$ is characteristic of the dislocation models of Cannon and Sherby.¹⁰ From the values of $1 < n < 3$ observed here, one is therefore inclined to assume more than one mechanism.

ACKNOWLEDGEMENT

This study was made possible by the generosity of Philips GmbH Research Laboratory Aachen (FRG) in affording me its hospitality and allowing me to use its facilities, as well as by the sabbatical leave granted to me by the University of Cologne. I am extremely obliged and grateful to those concerned. I also wish to express my warm thanks to Dr Wernicke and Dr Hennings for valuable suggestions and discussions, and to Mr Hüntten for his assistance with the experiments.

REFERENCES

1. Mostaghaci, H. and Brook, R. J., Kinetics of hot-pressing of BaTiO₃ ceramics, *Br. Ceram. Trans. J.*, **84** (1985) 203-6.
2. Graham, H. C., Tallen, N. M. and Mazdiyasn, K. S., Electrical properties of high-purity polycrystalline barium titanate, *J. Amer. Ceram. Soc.*, **54** (1971) 548-53.
3. DeVries, R. C., Lowering of Curie temperature of BaTiO₃ by chemical reduction, *J. Amer. Ceram. Soc.*, **43** (1960) 226.
4. Walker, B. E., Jr, Rice, R. W., Pohanka, R. C. and Spann, J. R., Densification and strength of BaTiO₃ with LiF and MgO additives, *Am. Ceram. Soc. Bull.*, **55** (1976) 274-80 and 284-5.
5. Sharma, N. C. and McCartney, E. R., Dielectric properties of pure barium titanate as a function of grain size, *J. Aust. Ceram. Soc.*, **10** (1974) 16-20.

6. Brandmayer, R. J., Brown, A. E., Di Vita, S. and Fischer, R. J., *Hot-pressing moulding of ceramic ferroelectric materials*, US Patent 2990 602, July 4, 1961.
7. Crayton, P. H. and Price, J. J., Prediction of effective isothermal hot-pressing temperature, *Am. Ceram. Soc. Bull.*, **63** (1984) 715–17.
8. Vieira, J. M. and Brook, R. J., Kinetics of hot-pressing: the semilogarithmic law, *J. Amer. Ceram. Soc.*, **67** (1984) 245–9.
9. Spriggs, R. M. and Dutta, S. K., Mechanisms of sintering during hot pressing and recent technological advances, *Mater. Sci. Res.*, **6** (1973) 369–94.
10. Cannon, W. R. and Sherby, O. D., Third-power stress dependence in creep of polycrystalline nonmetals, *J. Amer. Ceram. Soc.*, **56** (1973) 157–60.
11. Cannon, W. R. and Langdon, T. G., Creep of ceramics, part 1 mechanical characteristics, *J. Mat. Sci.*, **18** (1983) 1–50.
12. Nabarro, F. R. N., Deformation of crystals by the motion of single ions, in *Report of a Conference on the Strength of Solids*, University of Bristol, July 1947; Physical Society, London, 1948, 75–90.
13. Herring, C., Diffusional viscosity of a polycrystalline solid, *J. Appl. Phys.*, **21** (1950) 437–45.
14. Coble, R. L., Sintering crystalline solids. I. Intermediate and final state diffusion models. *J. Appl. Phys.*, **32** (1961) 787–92.
15. Coble, R. L., Sintering crystalline solids. II. Experimental test of diffusion models in powder compacts, *J. Appl. Phys.*, **32** (1961) 793–9.
16. Coble, R. L., Diffusion models for hot pressing with surface energy and pressure effects as driving forces, *J. Appl. Phys.*, **41** (1970) 4798–807.

Received 22 September 1986; revised version received 9 March 1987; accepted 20 March 1987