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# High Density Sintering of Pure Barium Titanate

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The techniques of slow sintering, addition of a volatile flux, and grain growth inhibition have been used to produce high density sintering in pure barium titanate. The use of carbon as grain growth inhibitor gave a density of 99% theoretical at 0.7$\mu$m grain size. This technique may be used for other suitable ceramics, when the proposed application requires improved physical properties. An extension of the procedure gives a range of electrically conducting ceramics.

## 1. Introduction

The dramatic improvements in the properties of alumina when it is sintered close to theoretical density suggest that there is considerable scope for improvement in many other ceramics. The technique used to produce high density alumina of the "Lucalox" type is based on the addition of about 0.1% magnesia. This procedure is specific to alumina [1, 2].

For other ceramics new methods must be devised. These should ideally avoid adding impurities, for it is often just when physical requirements are the most stringent that the highest purity is required. This is particularly so when specific electrical as well as other physical properties, such as high density, corrosion resistance, or thermal conductivity, are needed. The difficulty of producing dense, fine-grained ceramics increases with increasing purity because of the increased grain growth.

High temperature electrodes for magnetohydrodynamic generation, and ceramics for use as overhead power line insulators are cases in which conventional techniques for producing good densification are undesirable. It is for the latter use in particular [3] that the work described here was carried out. The techniques involved are however capable of much wider application. Three approaches to high densification were investigated; slow sintering, addition of fluxes, and grain growth inhibition, with special emphasis on avoiding contamination of the final material with impurities.

## 2. Experimental

### 2.1. Slow Sintering

The most obvious way to obtain high density with high purity material is to sinter for a long time at a relatively low temperature, in the hope that pore elimination will precede grain growth. Several workers have tried this method with high purity barium titanate, the material of immediate interest here [4-6]. The highest density recorded was 97% of the theoretical maximum of 6.02 g/cm$^3$ [4].

Efforts to improve upon this, using firing times of up to 200 h, with very precise temperature control, were unsuccessful. The use of more complex firing cycles, with prolonged soaks at several temperatures, and with very slow warm-ups, were also ineffective. Firing in vacuum had no effect on the densities achieved. (This does not seem to be the case with commercial grade barium titanate [7].)

The maximum density achieved, with National Lead "highest purity" grade barium titanate, was 96% of theoretical. Densities quoted in this paper are geometric, and therefore show total porosity. Densities measured using an immersion technique were identical with geometrical densities above about 95%. This indicated, as might be expected, that the remaining porosity was closed rather than open porosity.

Some high purity barium titanate was prepared

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from recrystallised barium titanium citrate [8] and spectroscopic analysis showed this to be purer than the National Lead material: it is expected to be very close to stoichiometry because of the method of preparation (see also section 2.2). This material could be fired directly to give 98% of theoretical density at 2 μm grain size. Unfortunately some batches gave a density of only 96%. This is attributed to variations in crystallite size and shape in the barium titanate, which was only prepared on an experimental scale.

## 2.2. Addition of Fluxes

It is standard practice in the manufacture of many technical ceramics to add a glassing or fluxing agent to promote sintering. The mobility of atoms at the grain boundaries is increased, and so the rate of sintering and of pore elimination is greater. As we are concerned here with the preparation of high purity material, it is necessary to select a volatile flux which can be "boiled off" at a higher temperature after sintering. Table I shows the fluxes selected for trial, together with the resultant densities.

These samples were fired for 8 h in air at 1430° C. Silica is a well-known non-volatile additive, and was used for comparison purposes. It has little effect under these conditions (cf [5]). The most effective was $NiCl_2$ which did not appear to react with the titanate, and formed what seemed to be a remarkable two-phase structure when added to excess (5%). However attempts to remove the $NiCl_2$ completely by subsequent heating were unsuccessful. 3% remained even after heating for 48 h at 1350° C in a vacuum of $2.10^{-6}$ torr. Since $NiCl_2$ was the most volatile of the materials tried this technique was abandoned.

High purity barium titanate is usually made by a precipitation process which tends to leave it $TiO_2$-rich. The result of adding $BaCO_3$ to compensate for this is particularly interesting, although it is probably confined to $BaTiO_3$ and similar materials.

A "microscopic" dispersion of $BaCO_3$ was achieved by first moistening the $BaTiO_3$ powder with $Ba(NO_2)_2$ solution, mixing in thoroughly, and then adding $NH_4HCO_3$ solution to form $BaCO_3$ in the required quantity. This technique gave a density of 5.72, compared with 5.86 for a dispersion of fine $BaCO_3$ powder in water. It is probable that the $BaCO_3$ reacts with $BaTiO_3$ and barium-rich phases in the $BaO/TiO_2$ system [10] to form a low-melting flux at the grain boundaries when it is present locally in high concentrations. Deviations from the formula $BaTiO_3$ at the grain boundaries can have an undesirable effect on the electrical properties. It was to avoid this problem that exactly stoichiometric $BaTiO_3$ was made from recrystallised barium titanium citrate, as described in section 2.1.

## 2.3. Grain Growth Inhibition

Insoluble impurities or precipitates at a grain boundary increase the energy required for grain boundary motion. Once the grains reach a certain size then grain growth practically ceases. This can allow sintering to proceed to virtual completion by the elimination of pores along grain boundaries if the stabilised grain size is sufficiently small. Inhibition of grain growth in $BaTiO_3$ has been reported for additions of ceria [11], samaria [6] and tantalum oxide $Ta_2O_5$ [5]. This inhibition was incidental to the modification of the electrical properties of the $BaTiO_3$ for which the additives were chosen. Unfortunately these materials cannot be removed after sintering.

It was therefore decided to try carbon as a grain growth inhibitor. The effect of carbon as a

TABLE I Effect of fluxes.

| Flux | Melting point (° C) | Temp. for vapour pressure of 1 torr [9] | 40 torr | 760 torr | Density for addition of 0.1 | 1.0 | 5.0 wt % flux |
|---|---|---|---|---|---|---|---|
| None | | | | | | 5.76 | |
| $SiO_2$ | 1720 | | Not volatile | | 5.70 | 5.74 | 5.71 |
| CdO | 1426 | 1000 | 1257 | 1559 | 5.69 | 5.68 | 5.60 |
| PbO | 890 | 943 | 1189 | 1472 | 5.71 | 5.60 | 5.55 |
| $BaCl_2$ | 925 | | | 1560 | 5.74 | 5.70 | 5.69 |
| KF | 880 | 885 | 1156 | 1502 | 5.68 | 5.64 | 5.59 |
| $CuCl_2$ | 498 | | | 1366 | 5.75 | 5.74 | 5.72 |
| $NiCl_2$ | 1001 | 671 | 821 | 987 | 5.75 | 5.80 | 5.89 |

grain growth inhibitor has been described previously, but in carbonyl iron [12], where it is probably a solution-precipitation reaction which may be related to the action of magnesia in alumina. The behaviour of carbon in a ceramic would be expected to differ from that in a metal like iron, in which it is partly soluble.

Carbon was selected here because of its inertness to and insolubility in $BaTiO_3$ in particular, and ceramics in general. It can be added as an organic compound dissolved in water, giving very good dispersion in the ceramic. The ceramic can then be sintered in vacuum, the organic material decomposing to give a deposit of carbon around the grains, inhibiting their growth. After sintering, the ceramic can be heated in air to oxidise the carbon, which is readily removed as CO and $CO_2$.

$BaTiO_3$ samples were made containing 0.025, 0.05, 0.1, 0.2, 0.4, 0.6 and 0.8 wt % sugar. The sugar was added as 7 wt % solution to the $BaTiO_3$ powder. One-gram samples were pressed in a two-free-piston stainless steel die at 40 tsi (0.04 kg/mm$^2$). The sugar solution acted as binder. They were then fired for up to 200 h at 1350° C in a vacuum of $2.10^{-6}$ torr. Sugar melts before decomposing, giving additional dispersion in the ceramic.

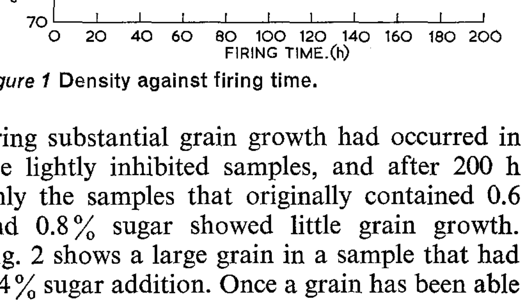

*Figure 1* Density against firing time.

Density as a function of firing time is shown in fig. 1. For clarity only the representative types with original contents 0.025, 0.4 and 0.8 % sugar (samples 2, 6, and 8) are shown. After 5 h firing substantial grain growth had occurred in the lightly inhibited samples, and after 200 h only the samples that originally contained 0.6 and 0.8 % sugar showed little grain growth. Fig. 2 shows a large grain in a sample that had 0.4 % sugar addition. Once a grain has been able to grow to a critical size because of a local absence of carbon, then the presence of carbon around nearby grains does not appear to inhibit effectively growth of the large grain. The grain continues to enlarge until it meets another large grain. The probability of there being areas with insufficient carbon to inhibit the initial grain growth is greatest in the more lightly inhibited material. As a large grain grows, the small voids between grains are eliminated and a few larger voids form in the large grain.

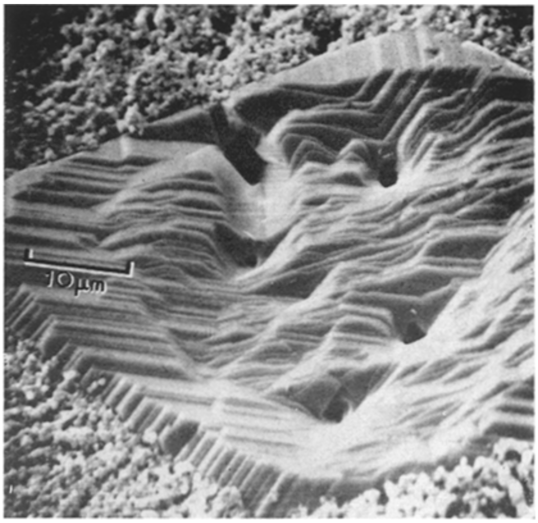

*Figure 2* A large grain in a sample with 0.4% sugar addition.

Samples could conveniently be examined with a scanning electron microscope after firing because the carbon made them good electrical conductors ($BaTiO_3$ is also partially reduced in vacuum, making it conduct). The small grains appear to be roughly spherical under the scanning electron microscope because of the effect of electron penetration. An internal surface, exposed by breaking a sample, had a very similar appearance to an external surface. The sample made with 0.025 % sugar achieved its maximum density, 96.5 % of theoretical, after 5 h sintering. Large grains then made up about 30 % of the observed surface area. The density then fell slowly with firing time because of grain growth and recrystallisation. After 50 h the surface showed more than 90 % large grains. The sample with 0.4 % sugar achieved its maximum density of 98 % of theoretical after 50 h, when large grains occupied about 5 % of the observed area. The density then fell in a similar way to that of sample 2 with 0.025 % sugar. This is a little surprising, since the carbon which is so effective in controlling grain growth in the first 50 h would be expected to inhibit further grain growth and recrystallisation compared with sample 2. There was however greater spread in the value for density after 200 h in samples with 0.4% sugar than in the other values.

Sample 8, with 0.8% sugar, reached the maximum observed value of 99% of theoretical density after 200 h. The virtually linear rise in density from 50 to 200 h is remarkable. After 200 h large grains only occupied about 1% of the surface area, while the mean grain size of the remainder was 0.7 μm, showing the effectiveness of the grain growth inhibition.

The carbon was removed from the samples by heating in air to 1000° C for ½ h. Sample 8, like the 98% dense 2 μm material prepared from barium titanium citrate (see section 2.1), showed the anomalously high permittivity found in fine-grained high-density $BaTiO_3$ [13]. Samples of type 8 could be heated in air to 1400° C for 1 h to give large-grained (80 μm) material with no measurable change in density. These samples, 2.5 mm thick, were translucent in ordinary daylight.

The effectiveness of small amounts of carbon in producing highly conducting $BaTiO_3$ ceramic suggests the extension of the solution additive technique when a conducting ceramic is required. A carbon-"doped" ceramic would only be useful in inert or reducing atmospheres. Preliminary tests were made using alumina (Linde A and B) and zirconia pressed with solutions of silver nitrate and platinic chloride. Because of lack of time, good firing conditions were found only for the silver-doped alumina. A dense strong alumina was made which was also highly conducting. Optimum firing conditions could certainly be found for the other systems.

## 3. Conclusions

Of the techniques tried, slow sintering, addition of a volatile flux, and grain growth inhibition using carbon, only the latter gave densities approaching theoretical. This technique was, however, very successful. The use of 0.8 wt % sugar, added as solution, gave a mean of 99% of theoretical density after firing, at a grain size of 0.7 μm, and reproducibility was good. The grain size could be increased to 80 μm at the same density by refiring in air. The technique can be applied to any ceramics which do not react with carbon, and can be fired initially in vacuum or non-oxidising atmosphere. Addition of a suitable compound in solution in the pressing process suggests a general technique for producing electrically conducting ceramics.

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