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# Importance of Homogeneous Composition in Sintering Behaviour of $Ba_2Ti_9O_{20}$ Ceramics

T. Jaakola, A. Uusimäki and S. Leppävuori

Microelectronics Laboratory, University of Oulu, SF-90570 Oulu, Finland

*SUMMARY*

*The densification behaviour of $Ba_2Ti_9O_{20}$ ($B_2T_9$) ceramics prepared from two different powder combinations—(i) $2BaCO_3 + 9TiO_2$; (ii) $2BaTiO_3 + 7TiO_2$—was investigated. It was observed that during calcination of the raw material mixture containing barium titanate ($BaTiO_3$), complete formation of $B_2T_9$, as well as good powder morphology, was readily obtained; in contrast, in the case of the powder containing barium carbonate ($BaCO_3$), good powder characteristics could only be obtained at the expense of achieving conversion to $B_2T_9$. Dilatometric measurements made at a constant heating rate showed that in the case of the powder starting with $BaCO_3$ the densification of the incompletely reacted powder slowed down temporarily at around 1250°C, while simultaneously, according to X-ray diffractometry (XRD), formation of $B_2T_9$ occurred.*

*Observations of the microstructure showed that anisotropic particle growth took place during this stage. It is argued that microstructural coarsening accounts for the observation that higher temperatures are necessary to densify the powders based on $BaCO_3$, as compared with those necessary to densify the powders based on $BaTiO_3$.*

## 1. INTRODUCTION

Single-phase $Ba_2Ti_9O_{20}$ ($B_2T_9$) is a ceramic having a high dielectric constant, low temperature coefficient of dielectric constant, and low dielectric loss, all of which combine to make it a useful material for microwave applications.[1,2] This compound was first reported by Jonker and Kwestroo[3] in their study of the $BaO$–$TiO_2$ system, and later O'Bryan *et al.*[4,5] determined its microwave properties and their dependence on



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processing parameters. Recently the crystal structure of $B_2T_9$ has been determined.[6]

Preparation of $B_2T_9$ ceramic by the conventional method involves the usual two processing steps, namely calcination of the starting materials and sintering to form the ceramic. During calcination the $B_2T_9$ phase partly forms, and the extent to which it does, and other factors, are known to influence the following sintering stage, the final microstructure and dielectric properties. For example, O'Bryan *et al.*[5] suggest that during the calcination stage barium-rich intermediates, such as $Ba_4Ti_{13}O_{30}$, $Ba_6Ti_{17}O_{40}$ and $BaTi_2O_5$, form; during the higher temperature sintering stage these can lead to the development of non-equilibrium liquid phases which can, in turn, concentrate impurities and cause microcracking, both of which are detrimental to dielectric properties. O'Bryan and Thomson[7] found it necessary to form some $B_2T_9$ during the calcination stage if a single-phase $B_2T_9$ ceramic is to develop in reasonable time during the sintering stage. Later studies[8] have revealed curvature of the $B_2T_9$ equilibrium phase boundary at high temperatures, and this is an additional complicating factor.

In more general terms densification and development of the microstructure during ceramic processing are affected by characteristics of the powder as well as the microstructure of the green compacts. Usually a combination of small particle size, non-agglomerated powder, and a homogeneous chemical composition is necessary to obtain an ideal sinterable powder.[9]

The primary aim of the present study was to determine the effect of incomplete formation of $B_2T_9$ during the calcination stage on the sintering behaviour, since this has immediate relevance to the manufacture of an important microwave dielectric. Initially, the dependence of $B_2T_9$ formation, for two starting materials, on both temperature and time was examined and the parameters for complete formation were determined. Subsequently, the shrinkage behaviour and evolution of the microstructure of the calcined powder compacts during sintering were examined.

## 2. EXPERIMENTAL PROCEDURE

The starting materials used for the preparation of $B_2T_9$ were reagent grade $BaCO_3$, $BaTiO_3$, and $TiO_2$ (anatase), the average particle sizes being in the range of approximately 1 $\mu$m, 1 $\mu$m and 0·1 $\mu$m, respectively. These oxides were mixed in two combinations: ($2BaCO_3 + 9TiO_2$) and ($2BaTiO_3 + 7TiO_2$). The mixing was carried out in distilled water for a period of 4 h in a plastic ball mill using agate balls. After drying the milled mixture, the powders were reacted at temperatures in the range 900 to 1200 °C, the particular temperature being dependent on the formulation. The reacted

powders were then reground and 1 wt% polyvinyl alcohol (PVA) added. Compacts were uniaxially pressed at 100 MPa into discs 10 mm in diameter and 4 mm thick. Sintering of the pressed discs was carried out at temperatures ranging from 1150 to 1380 °C for a period of 6 h, in air or oxygen.

Quantitative X-ray diffraction (XRD) analysis as described by Chung[10] was used to follow the formation of the $B_2T_9$ phase. The $2\theta$ values of the reflections used in the measurements were 29·3° for $B_2T_9$ and 30·1° for $BaTi_4O_9(BT_4)$; these were chosen since there was no overlapping and the reflections were quite intense. All the powders examined were found to contain only $B_2T_9$, and $TiO_2$ phases. It is likely that small amounts of phases such as $Ba_6Ti_{17}O_{40}$ were also present but, for sake of simplicity, their amounts were assumed to be negligible. Following Chung, the ratio $B_2T_9/BT_4$ was determined from which the weight fraction of $B_2T_9$ could be calculated with the help of the reaction equation ($2BT_4 + TiO_2 \rightarrow B_2T_9$).

Samples for the XRD measurements were prepared by rapidly heating the homogenised mixture (100 °C $min^{-1}$) to the desired reaction temperature and then rapidly cooling at the end of the predetermined reaction time. The powders were then thoroughly ground and the samples for the XRD measurements made according to the procedure described by Klug and Alexander.[11] To make intensity measurements of the peaks and background, Ni-filtered Cu–K$\alpha$ radiation and a counting time of 100 s were used.

The densification behaviour of the compacted powders was followed continuously using a high temperature dilatometer in which the shrinkage was transmitted to a linear voltage displacement transducer by an alumina push-rod, and the temperature monitored using a Pt–Pt/Rh thermocouple. Expansion of the alumina push-rod and specimen holder was compensated electronically. The specimens used for the dilatometric measurements were 10 mm in diameter and 25·4 mm thick, the heating rate was 5 °C $min^{-1}$ and the measurements were made in flowing oxygen. The evolution of the pore structure in the initial and intermediate stages of the sintering process was followed using a mercury porosimeter with a capability of measuring pore sizes between 120 and 0·006 $\mu$m. The microstructure of the partially and completely sintered specimens was examined using a scanning electron microscope, and the density values determined directly from weight and volume.

## 3. RESULTS

### 3.1. $B_2T_9$ formation and powder properties

The dependence of $B_2T_9$ formation on the temperature and time of reaction was studied in order to establish suitable reaction conditions for the two

powder mixtures under investigation, namely ($2BaCO_3 + 9TiO_2$) and ($2BaTiO_3 + 7TiO_2$). A reaction temperature of 1150 °C or higher was required for $B_2T_9$ formation to occur within a reasonable time span in the case of the mixture containing $BaCO_3$. At such temperatures a mixture of $BT_4$ and $TiO_2$ phases was quickly formed and, following reaction between the two components, produced $B_2T_9$. Formation of the $B_2T_9$ phase as a function of the reaction time at two different temperatures (1150 and 1200 °C) is shown in Fig. 1(a). From the curves it can be seen that in order to achieve $B_2T_9$ concentrations higher than 90 wt%, a reaction time greater than 24 h was required at 1150 °C, while at 1200 °C the corresponding time was 12 h.

Faster reaction kinetics occur for the mixture of $BaTiO_3$ and $TiO_2$, for which the reaction temperature for an equivalent reaction rate was lower by over 250°C. The reaction kinetics at the two temperatures are shown in Fig. 1(b). In order to achieve conversions of over 90 wt% at 1000°C, a time of 1 h was sufficient, while at 950 °C it was 4 h.

Table 1 shows the processing conditions selected for the preparation of the $B_2T_9$ powders, together with principal characteristics. The calcining schedules for powders A1 and B were chosen so as to obtain greater than 90 wt% conversion to $B_2T_9$. Examples of powder morphologies are shown in Fig. 2, and, as evident from Fig. 2(a), it proved difficult to grind A1 to a fine particle size with a narrow particle size distribution; better characteristics were obtained for the other powders.

Pore size distribution and specific surface area measurements were made on pressed compacts using the mercury porosimeter, the data showing that

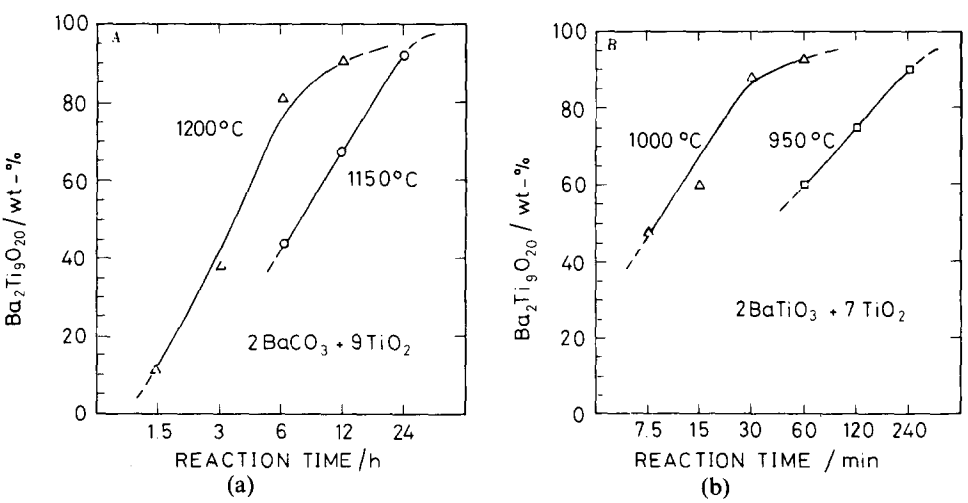


**Fig. 1.** Formation of $Ba_2Ti_9O_{20}$ from a mixture of (a) $BaCO_3$ and $TiO_2$, and (b) $BaTiO_3$ and $TiO_2$.

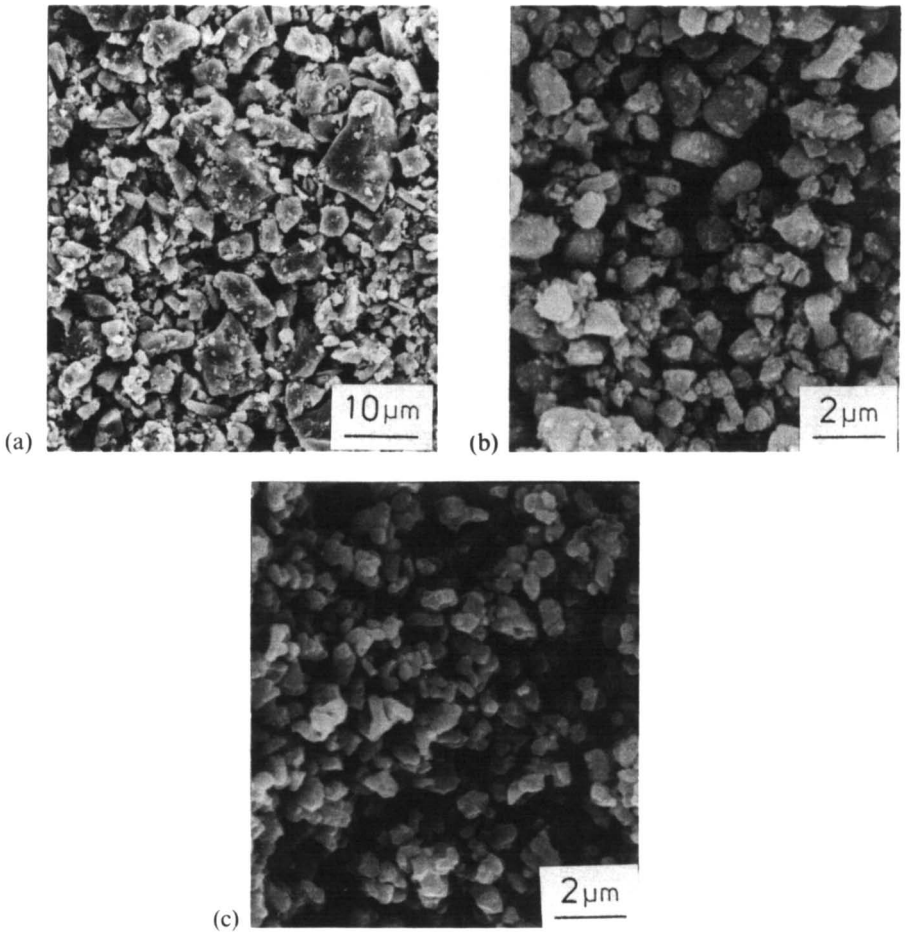


**Fig. 2.** SEM micrographs of calcined powders; (a) A1; (b) A2; (c) B.

the narrowest distribution was obtained with powder B and the broadest with powder A1. Specific surface area values for powders A2 and B were similar, and considerably higher than that of powder A1, as evident from Table 1. All these data appear consistent with Fig. 2.

### 3.2. Densification and development of microstructure

Figure 3 shows the densification of calcined powders measured by the dilatometer. Compared to the other powders, type A1, which had the largest particle size, required higher temperatures to achieve equivalent shrinkage. Powder compacts A2 and B showed similar initial densification rates as expected from their similar particle sizes. However, from approximately 1200 °C to 1300 °C the rate of densification of the partially reacted

**TABLE 1**
Processing Conditions and Powder Characteristics

| *Powder* | *Processing conditions* | | *Characteristics* | | |
|---|---|---|---|---|---|
| | *Temperature* $T_c/°C$ | *Time* $t/h$ | $S/m^2 g^{-1}$ | $d/\mu m$ | $B_2T_9/wt\%$ |
| A1 | 1 150 | 30 | 1·1 | 1–10 | >90 |
| A2 | 1 150 | 3 | 4·1 | 0·5–2 | 20 |
| B | 1 000 | 2 | 3·5 | 1 | >90 |

A = $BaCO_3 + TiO_2$ based powder
B = $BaTiO_3 + TiO_2$ based powder
$S$ = specific surface area
$d$ = particle size

powder, A2, decreased, and XRD showed this to be accompanied by the formation of $B_2T_9$.

The densities of compacts sintered for 6 h in air at various temperatures are shown in Fig. 4. As evident from Fig. 3, compacts of powder B sintered to a higher density at a lower temperature than compacts of either powder A1 or A2. In fact, the highest density achieved with B was at 1200 °C, there being a small decrease in density for compacts sintered to above this temperature. The density of powder compact A1 was comparable to that of the A2 compact despite the large difference in the starting particle sizes. At 1380 °C the densities of A1 and A2 powder compacts were comparable

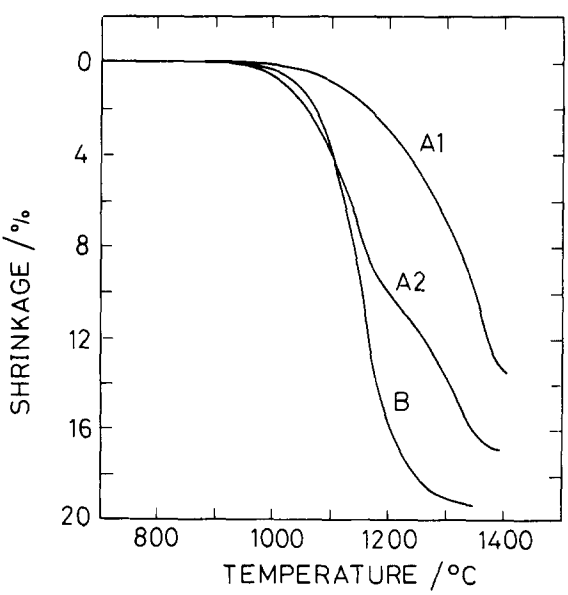


**Fig. 3.** Variation in non-isothermal shrinkage of compacts of powders. 'Green' compact densities: A1 = 62%, A2 = 56%, B = 52% (all based on theoretical density of $B_2T_9$).

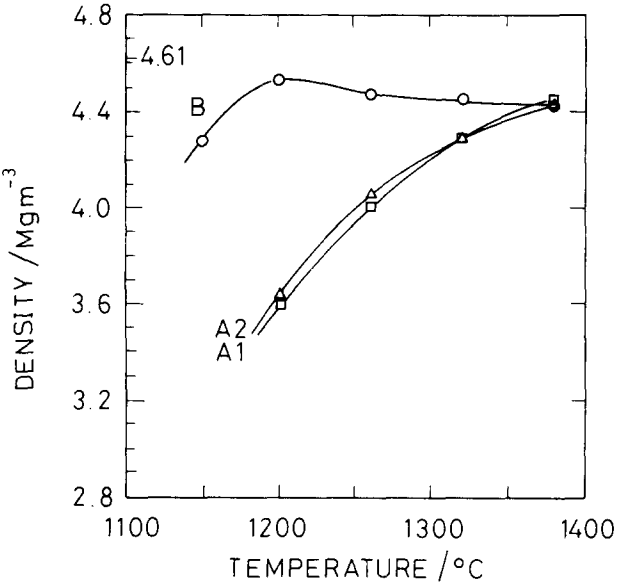


**Fig. 4.** Dependence of sintered density of powder compacts on temperature for a sintering time of 6 h in air. Theoretical density of $B_2T_9$ (4·61 Mg m$^{-3}$) is indicated.

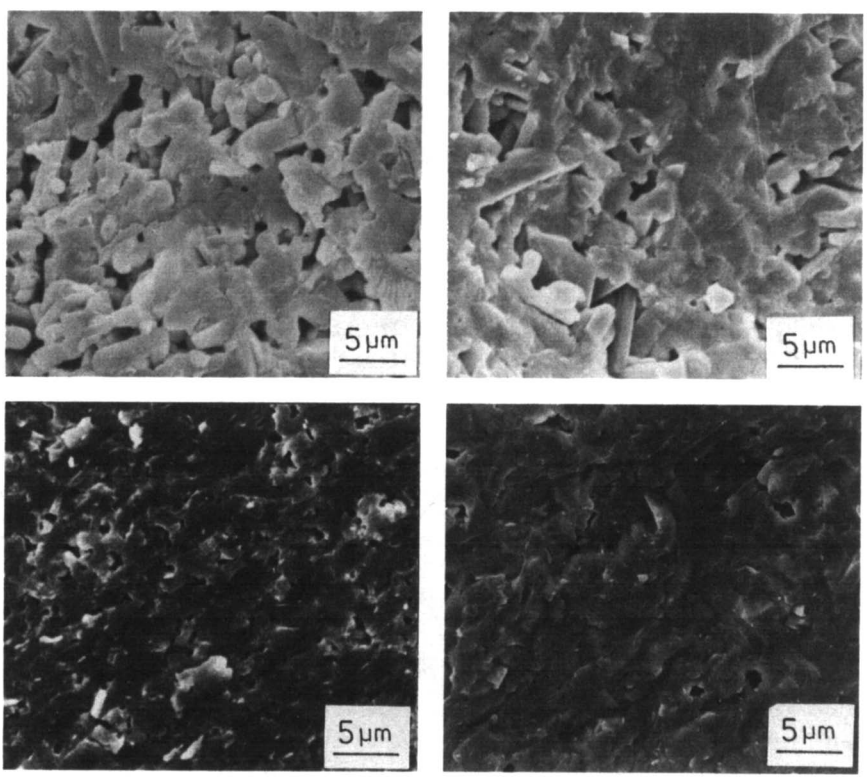


**Fig. 5.** Fracture surfaces of compacts A2 (above) and B (below) heated to temperatures 1200°C (left) and 1300°C (right).

to the density of the powder B compact. By sintering in an oxygen atmosphere rather than in air it was possible to attain higher final densities; for example, it was noted that at a temperature of 1380 °C and for compact A2, the density increased from 96% to 98% of theoretical.

In order to study the evolution of microstructure during densification, compacts were heated to temperatures of 1200 °C and 1300 °C using a constant rate of heating (5 °C $min^{-1}$) followed by rapid cooling. Fracture surfaces of the sintered ceramics are shown in Fig. 5. A significant difference between the structures is apparent and evidently related to the slowing down of the densification observed in Fig. 3. It can be seen that the pore size of the ceramic from powder B is significantly smaller than that from A2, and also that the ceramic sintered at 1300°C contains inhomogeneously densified regions where some elongated grains are visible.

## 4. DISCUSSION

The object of calcining the starting materials in ceramic processing is to obtain a chemically homogeneous material which, in addition, possesses the property of easy grindability to a fine particle size having narrow particle size distribution; this usually ensures good sinterability. Reaction to a homogeneous calcine is desirable since chemical homogenisation occurring simultaneously with sintering may disturb the process of densification.[12] In the case of $B_2T_9$ prepared from $BaCO_3$ with $TiO_2$ it was difficult to obtain both the above characteristics. High reaction rates required a high temperature or a long time span which led to poor grindability of the calcined powders, as can be seen by comparison of Figs 2(a) and 2(c). Characteristics closest to the ideal were attained with the $B_2T_9$ powder prepared from a mixture of $BaTiO_3$ with $TiO_2$. This was, of course, due to the much lower temperature that was required for complete reaction to occur and consequently to the formation of a relatively soft calcine. Additionally, compacts formed from this powder had the narrowest pore size distribution, which is important for achieving high density during sintering.[13]

The very significantly lower reaction temperature for the $BaTiO_3$ and $TiO_2$ raw material mixture compared to that for the $BaCO_3/TiO_2$ mixture (Fig. 1) was surprising. A possible explanation is that because the $BaTiO_3$ of the former mixture is closer to $B_2T_9$ in Ti content than $BaCO_3$, the diffusion distances involved to effect the solid state reaction are relatively short; clearly such conditions favour the development of a homogeneous ceramic. A further reason might be the formation of the intermediate $BT_4$, when $BaCO_3$ is one of the starting materials. Because the kinetics of $BT_4$

formation are known to be faster than those for the formation of $B_2T_9$,[14] the development of the mixture $BT_4 + TiO_2$ would occur prior to that of $B_2T_9$. This would be especially true were there to be incomplete mixing of the starting materials, possibly because of the presence of agglomerates. This effect was observed when $BaCO_3$ was one of the starting materials, since a nearly complete reaction to a mixture of $BT_4 + TiO_2$ intermediates preceded the formation of $B_2T_9$, which then occurred according to the reaction equation ($2BT_4 + TiO_2 \rightarrow B_2T_9$). The $TiO_2$ content at the onset of this reaction was about 10 vol% and so it is apparent that the diffusion distances increase as the reaction proceeds. It is known[7] that if complete ($BT_4 + TiO_2$) formation is allowed to occur, by calcining for 3 h at 1100 °C, then long times are required for single-phase $B_2T_9$ formation, even at a temperature of 1400 °C.

The slowing down of the densification rate measured for the incompletely reacted powder at around 1250 °C, and the observed simultaneous completion of the formation of $B_2T_9$ indicates that these processes are related.

The nature of the process occurring in an incompletely reacted $B_2T_9$ compact becomes clear from Fig. 6, where a series of samples which were heated for different times at a temperature of 1150 °C are shown. Strongly anisotropic grain growth was observed to take place. The uniform equiaxed particles of the starting compact changed to particles with a relatively high aspect ratio. The phenomenon was not surface-dependent since the same effect is evident in fracture surfaces. According to the XRD data the formation of $B_2T_9$ was completed after 320 min. Densification of the compacts was slight but the average pore size increased significantly from 0·5 $\mu$m after 5 min to 1·3 $\mu$m after 320 min.

On the basis of these observations an explanation for the anomalous densification behaviour is suggested. The solid state reaction ($2BT_4 + TiO_2 \rightarrow B_2T_9$) that occurs simultaneously with the densification causes the particle size and the pore size to increase, which in turn decreases the driving force for further densification. The structure of the compact becomes coarser and higher temperatures are then required for densification to proceed further. This effect could explain the quite similar densification data in Fig. 4, obtained for compacts A1 and A2, despite the very different starting powder particle sizes.

With powder B the coarsening of the structure of the compacts was not a problem and so attaining a high density even at a temperature as low as 1200 °C was possible; surprisingly, this is lower than what appeared to be the minimum (1275 °C) necessary to achieve full density in an interesting study of the continuous hot-pressing of $B_2T_9$ prepared from $BaCO_3$ and $TiO_2$.[15] The decrease in the final densities observed for the compacts of B as the sintering temperature was increased is most probably due to the

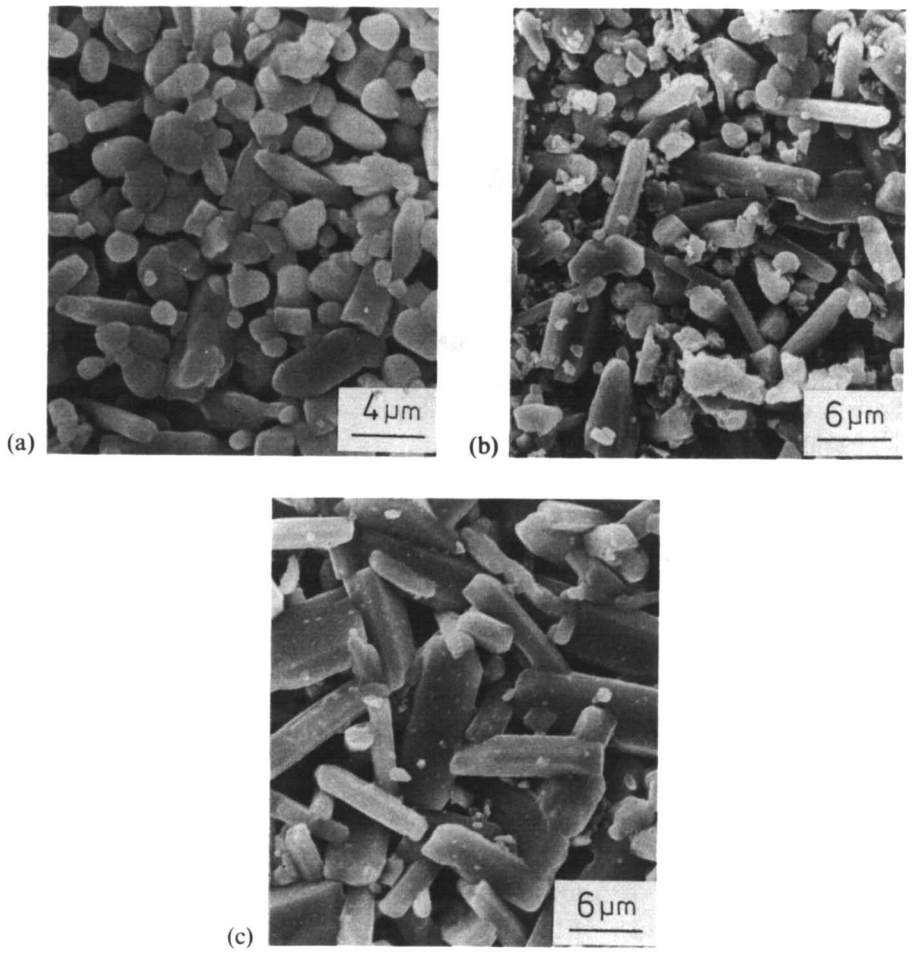


**Fig. 6.** Surfaces of compacts of powder A2 heated at 1150°C: (a) for 5 min; (b) for 80 min; (c) for 240 min. Densities of compacts after these time periods were 62%, 65% and 66% of the theoretical values, respectively.

coalescence of the pores at the grain boundaries which occurs simultaneously with grain growth.

## 5. CONCLUSION

The results of the study indicate that in fabricating $B_2T_9$ ceramics from powders having particle sizes of approximately 1 $\mu$m, the compositional homogeneity of the powder has a considerable effect on densification behaviour. In chemically inhomogeneous powders, completion of formation of the $B_2T_9$ phase, which occurred during densification, was found

to be accompanied by microstructural coarsening. This is believed to be the main reason for the observed decrease in densification rate and for the considerably higher sintering temperatures required.

By using as starting powders $BaTiO_3$ and $TiO_2$ instead of $BaCO_3$ and $TiO_2$, it was possible to obtain a homogeneous $B_2T_9$ powder that sintered to a density of 98% of theoretical at a temperature as low as 1200 °C.

## ACKNOWLEDGEMENT

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