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Influence of stoichiometry and impurity on the sintering behaviour of barium titanate ceramics

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The influence of stoichiometry, i.e. Ba/Ti ratio, and impurity on the densification of $BaTiO_3$ were investigated. The $BaTiO_3$ powders were prepared by conventional calcination of $BaCO_3$ and TiO_2. The stoichiometric ratios (Ba/Ti) were in the range 0.99 to 1.005. Impurity effects on the sintering behaviour were investigated with different purities of raw powders. The sintering behaviour of $BaTiO_3$ has been studied extensively but an understanding of stoichiometric effects on densification is still incomplete. An excess of TiO_2 lowered the onset temperature of sintering (initial state of sintering – 3% shrinkage). These results indicate that stoichiometric variation of $BaTiO_3$ affects the initial state of sintering. The rate of densification for a Ti-rich sample was considerably faster than that for a Ba-rich sample. It was a so-called "activated" sintering. The TiO_2 excess reacts with $BaTiO_3$ to form $Ba_6Ti_{17}O_{40}$, which forms with $BaTiO_3$ a eutectic melt at 1320 °C. The liquid phase, however, enhanced grain growth, not densification.

1. Introduction

Numerous studies of the sintering of barium titanate have been reported in the ceramic literature [1–4]. Powder purity, particle size, processing and sintering procedures used have varied widely, and the literature is filled with contradictory conclusions [5]. To investigate the reasons for the contradictory conclusions, we examined the effects of stoichiometry and impurity on the sintering behaviour simultaneously. Dilatomteric curves were used to study the whole procedure of the densification.

The Ba:Ti ratio of $BaTiO_3$ is an important factor which has been shown to dramatically influence microstructural development in high-purity $BaTiO_3$. An excess of BaO typically inhibits grain growth while excess TiO_2 enhances grain growth [6]. In a study involving a small excess of BaO or TiO_2 ($0.995 < Ba/Ti < 1.005$), Sharma *et al.* [7] reported a solubility limit of < 0.1 mol % TiO_2 in $BaTiO_3$ with increased TiO_2, resulting in the formation of a $Ba_6Ti_{17}O_{40}$ second phase [8]. This eutectic melt affects the sintering behaviour because of liquid phase formation at grain boundaries. Impurity effects can also significantly affect both sintering behaviour and properties. When present, Al_2O_3 and SiO_2 impurities can contribute to liquid phase formation at the grain boundary and enhance densification and grain growth [9, 10]. The purpose of this study is to investigate the sintering behaviour and the microstructure development with stoichiometry and impurity.

2. Experimental procedure

The $BaTiO_3$ powders used in this study were prepared by conventional calcination of $BaCO_3$ and TiO_2. The stoichiometric batches were prepared by mixing equimolar amounts of $BaCO_3$ and TiO_2, and non-stoichiometric mixtures were prepared by changing the amount of either TiO_2 or $BaCO_3$. The Ba/Ti ratios and the label numbers are listed in Table I. The difference between the A-series and B-series is in their purity. A-series powders used high-purity TiO_2 (99.9%) and the B-series used low-purity TiO_2 (99%). Processing of the powders involved wet milling for 24 h in polyethylene jars using a ZrO_2 medium. The slurries were dried and calcined at 1200 °C for 2 h in air. The average particle sizes of calcined powders were 2 μm. There were no differences in average particle size with composition variations. The powders were isostatically pressed at 120 MPa. The pellets were sintered at 1280–1400 °C for 0–4 h in air (0 h means without holding at the sintering temperature). A dilatometer was used to investigate the process of densification. The heating rate of the dilatometer was $5\,°C\,min^{-1}$ and it was held at 1400 °C for 1 h in air. The densities of pressed and sintered compacts were measured geometrically and by using the Archimedes method in a liquid medium. The polished and chemically etched surfaces of the samples were examined using an optical microscope and a scanning electron microscope (SEM). The grain sizes were determined by a line-intercept method.

3. Results

3.1. Densification of $BaTiO_3$

All the samples were examined by the X-ray diffraction method, which indicated that neither the Ba-rich

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TABLE I Powder compositions

Label number		Ba/Ti ratio
A-samples	B-samples	
A-1	B-1	0.990
A-2	B-2	0.995
A-3	B-3	1.000
A-4	B-4	1.005

TABLE II Impurity analysis of calcined powders

	Constituents (p.p.m.)				
	Pb	Mg	K	Si	Al
A-samples	< 50	20	300	73	400
B-samples	< 50	11	550	88	810

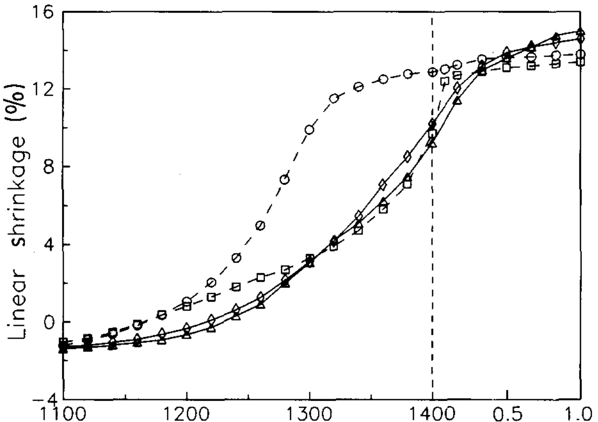

Figure 1 Shrinkage curves of A-samples during heating to isothermal sintering at 1400 °C: (○) A-1, (□) A-2, (△) A-3, (◇) A-4.

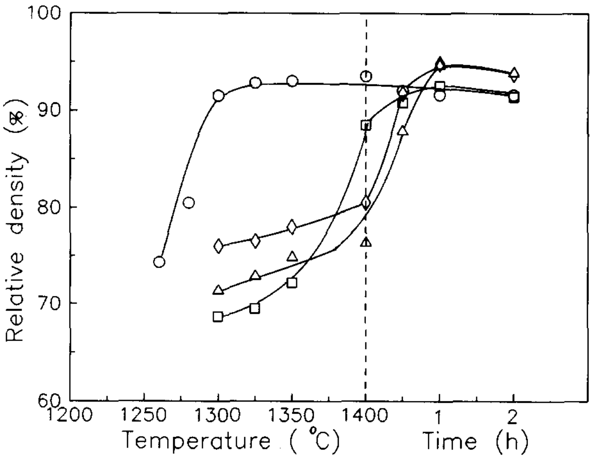

Figure 2 Variation of sintered densities during heating to isothermal sintering at 1400 °C (for A-samples): (○) A-1, (□) A-2, (△) A-3, (◇) A-4.

nor the Ti-rich samples contained any second phases.

Fig. 1 shows the shrinkage curves of A-samples with increasing temperatures and time. It is observed that the shrinkage rates were changed with composition variations. The densification rate of the Ti-rich sample (A-1) is faster than for the other samples (A-2, A-3 and A-4). It is well known that the small excess of TiO_2 reacts with $BaTiO_3$ to form $Ba_6Ti_{17}O_{40}$, which forms with $BaTiO_3$ a eutectic melt at 1320 °C [8]. Many researchers [8, 11, 12] have reported that the liquid phase promoted densification and grain growth of the $BaTiO_3$. However, the densification of the Ti-rich sample (A-1) was promoted at a lower temperature than the eutectic temperature. When the sintering temperature reached the eutectic temperature, further densification was not promoted as shown in Fig. 1. However, the densification of stoichiometric (A-3) and Ba-rich samples (A-4) continued at more elevated temperatures (1400 °C). The measured relative densities are shown in Fig. 2. The results of Fig. 2 agree well with those of Fig. 1. The onset temperature of sintering for the Ti-rich sample (A-1) is lower than for the others (A-2, A-3 and A-4). The excess of TiO_2 lowered the onset temperature of sintering and also promoted the densification rate, as shown in Figs 1 and 2.

In a study involving a small excess of BaO or TiO_2 ($0.990 < Ba{:}Ti < 1.005$), Sharma *et al.* [7] reported a solubility limit of < 0.1 mol % TiO_2 in $BaTiO_3$, with increased TiO_2 resulting in formation of a $Ba_6Ti_{17}O_{40}$ second phase [8]. Therefore, the Ti-rich samples (A-1 and A-2) are outside the solubility limit. However, the densification rate of the A-1 sample was different from that of the A-2 sample. Therefore, the reason for the enhancement of densification rate with a small excess of TiO_2 in $BaTiO_3$ cannot be explained by the vacancy model (increasing oxygen vacancy or barium vacancy).

The presence of SiO_2 and Al_2O_3 in Ti-rich $BaTiO_3$ compositions has been found in the literature [10] to contribute to the formation of the liquid phase at 1240 °C. As shown in Table II, however, the content of SiO_2 is very small (< 90 p.p.m.). If this content could form the liquid phase, the densification of 0.5 mol % TiO_2 excess composition (A-2) must be enhanced. However, the results (Figs 1 and 2) do not agree with that hypothesis.

The shrinkage curve of the Ti-rich sample (A-1) and those of others were already different at 1200 °C (Fig. 1). These results show that a TiO_2 excess affects the initial state of sintering below the liquid formation temperature. Unfortunately, the reasons for these results are not clear, but this phenomenon is similar to so-called "activated" sintering in metallic systems [13]. It is known that the densification rate in activated sintering is accelerated by a small addition of an element, but it has not been explained precisely [14].

Impurities can also significantly affect sintering behaviour. Figs 3 and 4 show the shrinkage curves of B-samples which contained many impurities and their relative density, respectively, with sintering temperature and time. The impurities which possibly form the liquid phase are listed in Table II. These impurities should cause a lowering of the eutectic temperature of $BaO–TiO_2$ (1320 °C). The following systems are known:

$BaTiO_3$–SiO_2	(1250 °C [15])
$BaTiO_3$–K_2SiO_3	(900 °C [16])

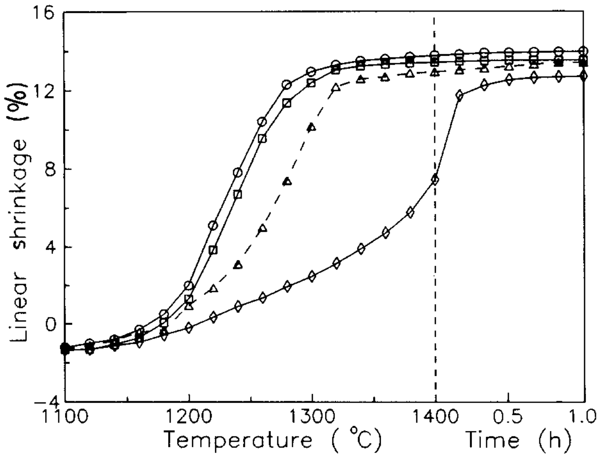

Figure 3 Shrinkage curves of B-samples during heating to isothermal sintering at 1400 °C: (○) B-1, (□) B-2, (△) B-3, (◇) B-4.

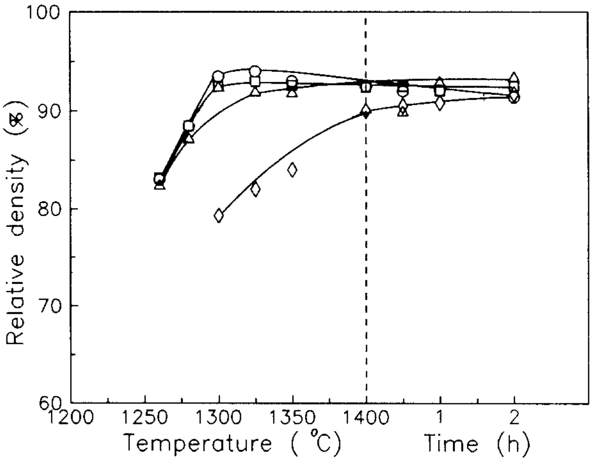

Figure 4 Variation of sintered densities during heating to isothermal sintering at 1400 °C (for B-samples): (○) B-1, (□) B-2, (△) B-3, (◇) B-4.

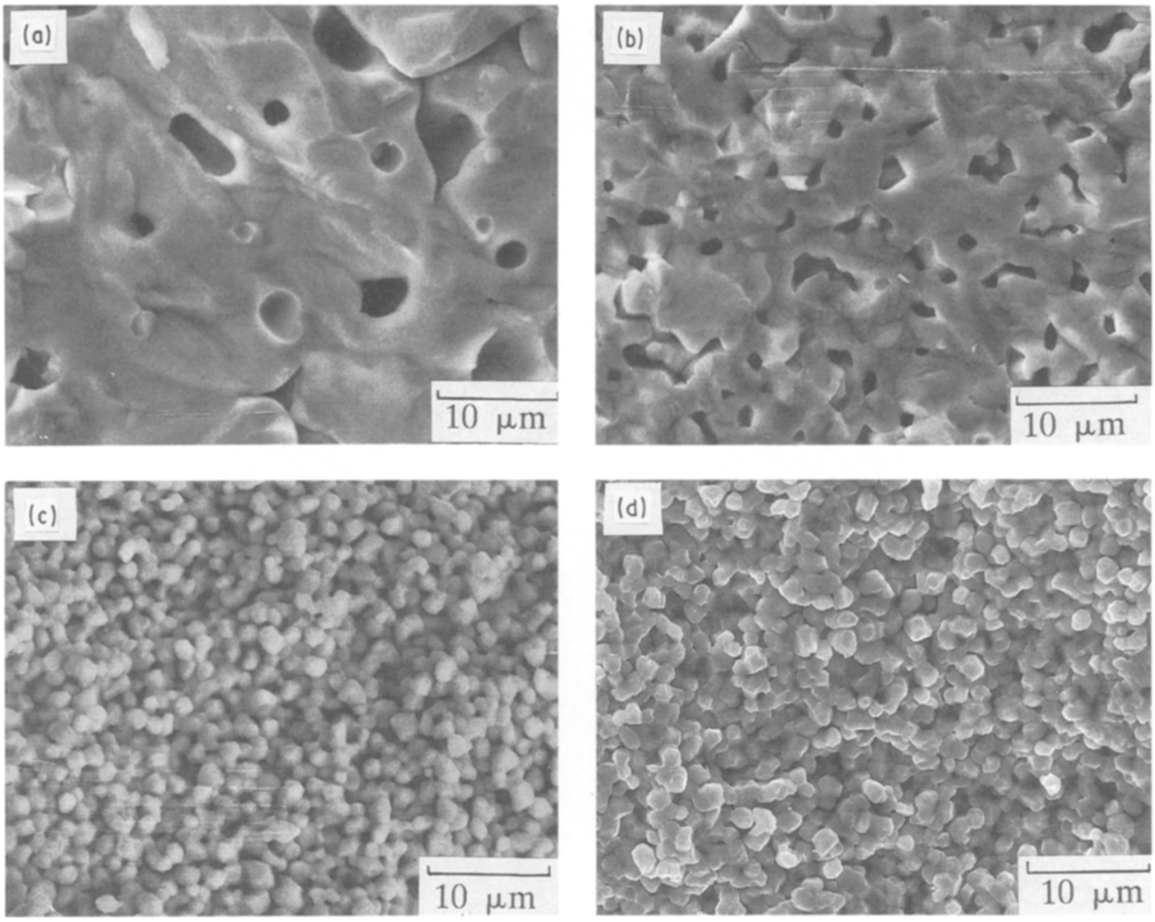

Figure 5 Fracture surfaces of A-samples sintered at 1400 °C without hold: (a) A-1, (b) A-2, (c) A-3, (d) A-4.

As shown in Table II, the amounts of K and Al are different between A-samples and B-samples, but the amounts of Si are the same. As shown in Figs 1 and 3, however, there are some differences in the sintering behaviour. Densification was promoted by impurities although the Ba/Ti ratios were the same. For B-samples, the onset temperature of sintering (as for A-samples) was lowered with increasing TiO_2 excess in $BaTiO_3$. It is believed that the other impurities (K, Al, etc.) in B-samples affect the sintering behaviour, but the role of TiO_2 excess is still incomplete.

In the case of the Ba-rich sample (B-4), the excess of BaO in $BaTiO_3$ (in spite of impurities present) inhibited the densification, but these results are contradictory to the results of Tsai-Fa Lin *et al.* [17]. They suggested that an excess of BaO in La-doped $BaTiO_3$ improved the densification by defect formation (1 mol % BaO excess). However, it is well known that the solubility limit of BaO in $BaTiO_3$ is very low: Hu *et al.* [18] reported that the solubility of BaO in $BaTiO_3$ had been determined to be no more than 100 p.p.m. They observed a second phase comprising barium orthotitanate, Ba_2TiO_4, for all samples having Ba/Ti ratios > 1.001. It is believed that orthotitanate inhibits the densification.

3.2. Grain growth in $BaTiO_3$

The dielectric properties of sintered $BaTiO_3$, in fact, exhibit a strong dependence on grain size. For grain size < 1 μm, anomalously high room-temperature permittivity values are obtained along with a general broadening and flattening of the permittivity peak at the Curie temperature [19]. Therefore, grain size control of the sintered bodies is very important.

Fig. 5 shows the fracture surfaces of A-samples sintered at 1400 °C without holding. As shown in Figs 1 and 2, the densification for the Ti-rich sample (A-1) alone was over by 1300 °C. Accordingly, the grain growth of the A-1 sample was enhanced by eutectic melting (Fig. 5a). On the other hand, the grain growth of the stoichiometric (A-3) and Ba-rich (A-4) samples was inhibited by pore drags (Fig. 5b, c and d). Although these compacts were heated to 1400 °C, the densifications were not over.

In the case of B-samples which contained a few impurities, however, the grains grew large (Fig. 6). These results could be explained on the grounds that the impurities not only improved densification but also formed a small liquid phase at the grain boundary. Because the diffusivities of cations are higher through the liquid phase than through the lattice, grain growth can be enhanced by a small liquid phase at the grain boundary. However, these explanations need more detailed observation of the liquid phase at the grain boundary using a scanning transmission electron microscope.

When the samples have the same Ba/Ti ratio but only different purities (A-1 and B-1), the microstructure variations with sintering temperatures (without holding) are as shown in Figs 7 and 8, respectively. These results indicate that the impurities enhanced grain growth (Fig. 8).

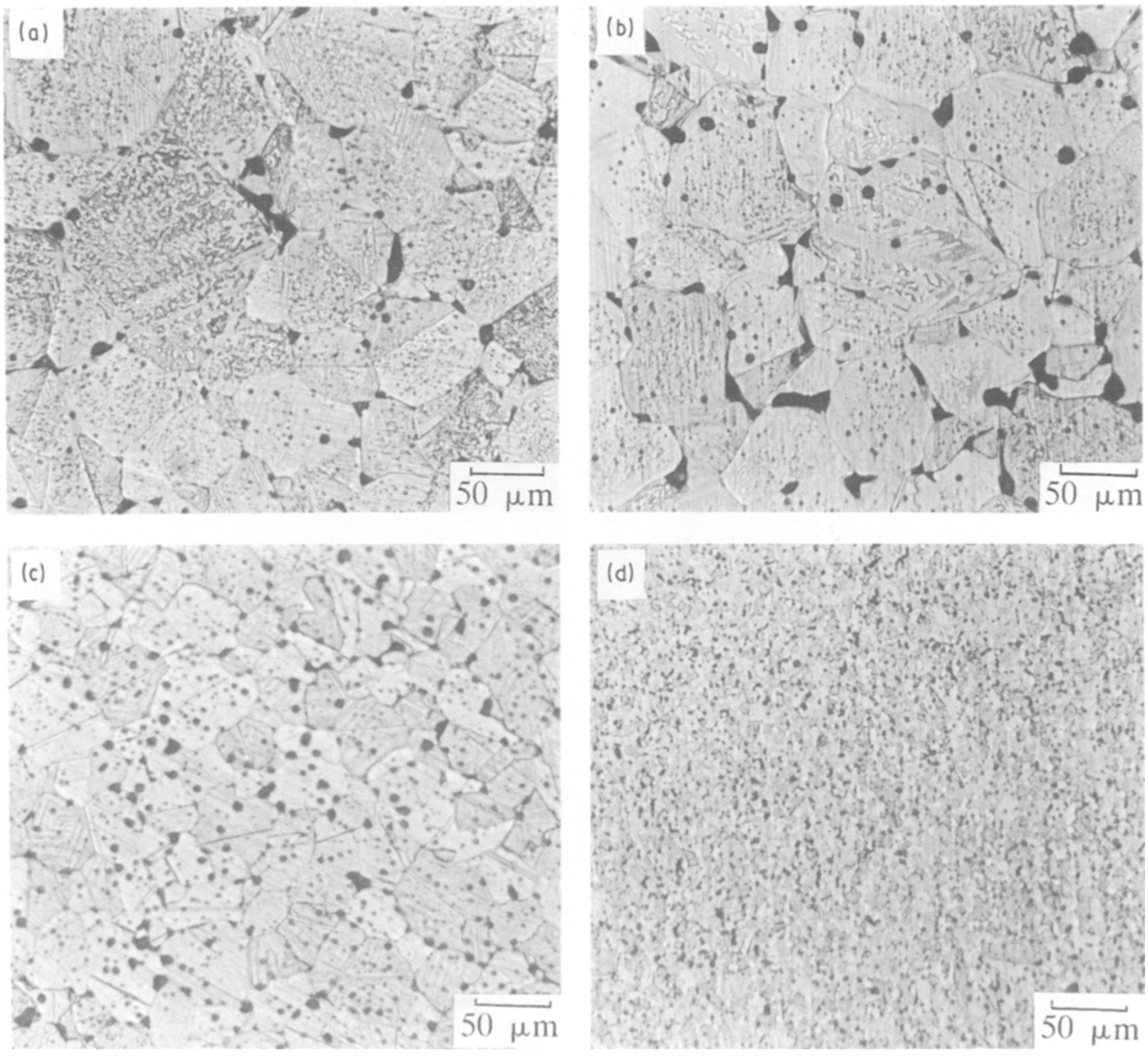

Figure 6 Microstructures of B-samples sintered at 1400 °C without hold: (a) B-1, (b) B-2, (c) B-3, (d) B-4.

Many authors [8, 11, 12] have suggested that a eutectic melt improves densification by liquid-phase sintering in $BaTiO_3$ above 1320 °C, but it was observed here that the eutectic melt inhibited rather than promoted further densification above 1320 °C. As shown in Figs 7 and 8, many pores were trapped in grains and large pores were formed at the grain boundary due to fast grain growth above 1320 °C.

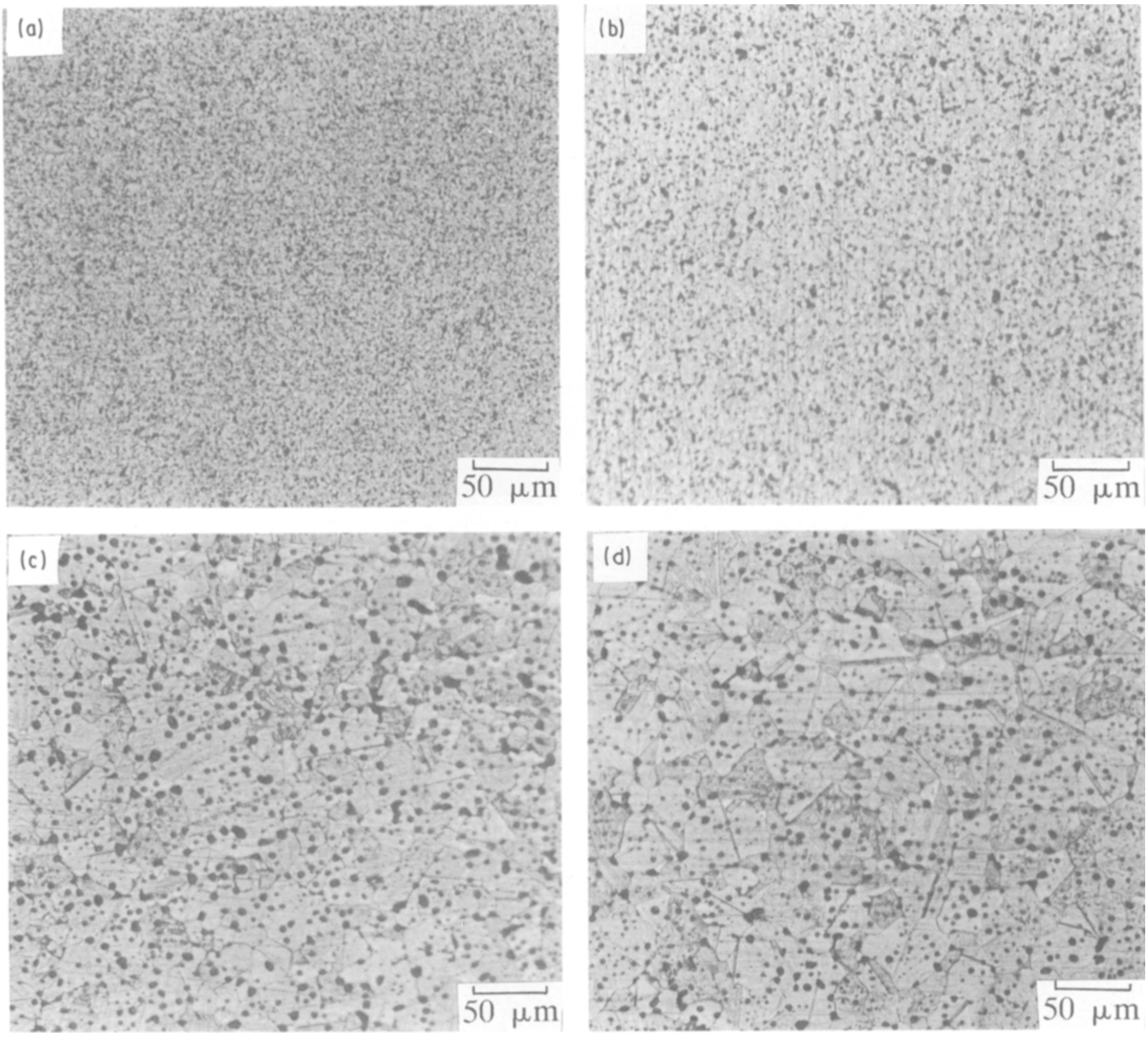

Figure 7 Microstructures of A-1 sample sintered at different temperature without hold: (a) 1300 °C, (b) 1325 °C, (c) 1350 °C, (d) 1400 °C.

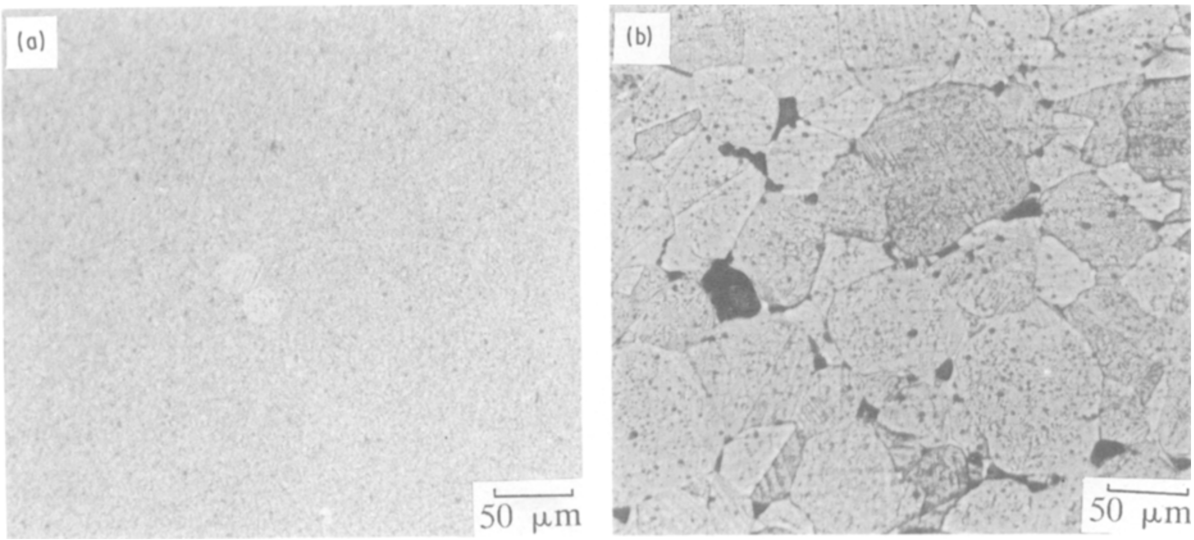

Figure 8a, b

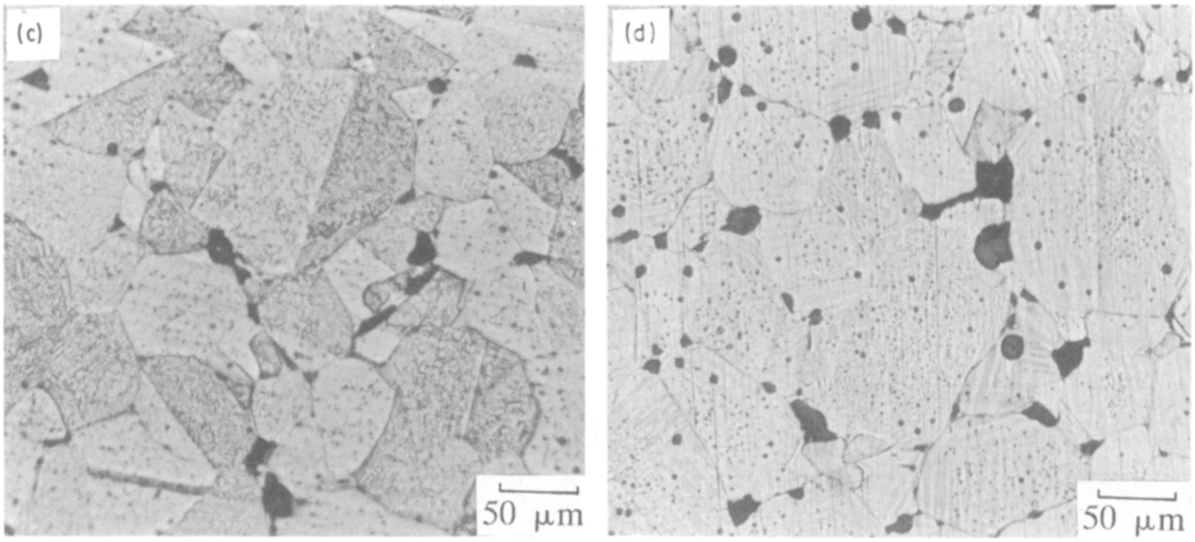

Figure 8 Microstructures of B-1 sample sintered at different temperatures without hold: (a) 1300 °C, (b) 1325 °C, (c) 1350 °C, (d) 1400 °C.

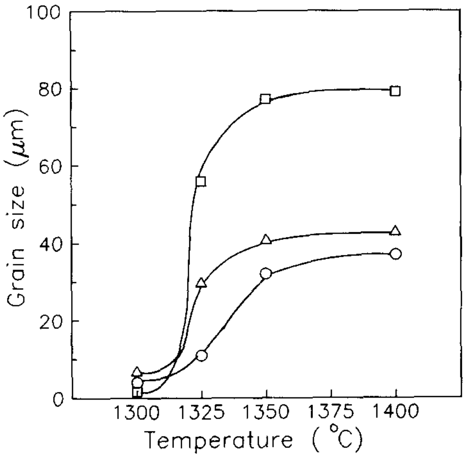

Figure 9 Variation of grain size with sintering temperature: (○) A-1, (□) B-1, (△) B-3.

Fig. 9 shows the grain growth with increasing the sintering temperature without holding. The grain growth of $BaTiO_3$ was enhanced by TiO_2 excess and by impurities. Above the eutectic temperature, though without holding at the sintering temperature, the grain growth was enhanced tremendously.

4. Conclusions

A TiO_2 excess in $BaTiO_3$ lowered the onset temperature of sintering and promoted the densification rate, but the reasons for these results were not clarified. Impurities also improved densification below 1320 °C. Above 1320 °C, fast grain growth occurred due to eutectic melting and the effects of impurities. This eutectic melt inhibited rather than promoted further densification due to the pores trapped in grains and the large pores formed at grain boundaries. In the case of BaO excess, the densification was inhibited by orthotitanate Ba_2TiO_4 (in spite of impurities being present).

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