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THE EFFECT OF SINTERING TIME ON THE DENSIFICATION OF PURE NANO-SIZED BATIO$_3$

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ABSTRACT

Sintering of nano-sized pure $BaTiO_3$ was carried out at 1220^0C between 30 to120 minutes. From the density vs sintering time curve, three stages of densification were identified followed by a stage of dedensification, based on the rate of densification. In the first stage, very high rate of densification was observed up to the sintering time of 40 minutes. In the second stage, the rate of densification started to decrease with increase in sintering time and this trend continued up to 90 minutes. In the third stage, the rate of densification was really low which continued up to the sintering time of 110 minutes. Finally, in the fourth stage, the rate of densification showed a negative trend and the overall density was lowered due to dedensification. As the sintering time was increased from 30 to 120 minutes, the grain size showed an increasing trend.

Keywords: Barium Titanate, Densification, Dedensification.

1. INTRODUCTION

There is an increasing demand for the use of high permittivity ferroelectric materials in microwave devices. High-permittivity ferroelectric materials will assist in the material selection for decoupling capacitors currently utilized in computer packaging. Decoupling capacitors are used to neutralize line inductance by placing the decoupling capacitors near the silicon chip to reduce spurious switching in signal lines. [1-3] Barium titanate (BT) is one of the most important dielectric materials for the electronic devices, such as MLCC (Multi Layer Ceramic Capacitor). The thickness of the barium titanate thin film in MLCC has become thinner and reached about 1 μm. Further downsizing is required for the higher performance. For this reason, we should consider the densification of fine grained BT.

Depending on the applications, tailored electrical properties can be obtained by adding adequate dopants and by controlling the final grain size. [4] Accordingly, densification and grain-growth mechanisms in $BaTiO_3$ have been thoroughly investigated. [5-6] Densification is generally improved by liquid-phase sintering [7] at temperatures $>1317^0$C for titanium-rich BaTiO3 or at lower temperatures with sintering aids. [8] Anomalous grain growth is frequently encountered during the sintering of undoped $BaTiO_3$ [9] or $BaTiO_3$ that has been doped below the critical dopant concentration. [10] As the sintering temperature or sintering time increases, a dedensification step can occur, which has been reported in numerous studies. [11-13] During natural sintering at temperatures $>1310^0$C, the microstructure at maximum density always exhibits a bimodal grain-size distribution with large grains (>10 μm) in a fine-grained porous matrix. This suggests the existence of a correlation between the isotropic abnormal grain growth and the dedensification step. This phenomenon seems to be strongly correlated with the occurrence of a liquid phase. In this case dedensification was caused by an effect of tensile stresses that was induced by the growth of a rigid, interconnected network of large grains.

[14]According to theory, the equation for the rate of growth of neck area between particles is:

$$\frac{x}{r} = \left(\frac{40\gamma a^3 D^*}{KT}\right)^{1/5} r^{-3/5} t^{1/5} \quad (1)$$

Here, x is half the length of neck region between particles, r is the radius of the particle, t is the sintering time, D^* is the self-diffusion coefficient etc. The equation for rate of densification is:

$$\frac{\Delta V}{V_o} = 3\left(\frac{20\gamma a^3 D^*}{2^{1/2} KT}\right)^{2/5} r^{-6/5} t^{2/5} \quad (2)$$

V_o is the starting volume and $\triangle$V is the change in volume, a^3 is the volume of the diffusing vacancy.

The purpose of this paper is to clarify the stages of densification process during the sintering of pure $BaTiO_3$ below 1310^0C where liquid phase is absent. For this purpose, the sintering time was varied over a long range to understand the mechanism of densification. Beside studying the densification process, the dedensification phenomenon and the effect of sintering time on grain growth will also be discussed.

2. EXPERIMENTAL PROCEDURE

Starting material for the experiment was nano sized (~100 nm) pure barium titanate powder. At first, barium titanate powders were milled for 18 to 20 hours. After milling, the powders were dried and binder PVA was added. Then powder were pressed into discs using pressure of ~ 300MPa using a hydraulic press.

For densification, single stage sintering was used. For all sintering cycles, samples at first were heated to 550^0C and holding at this temperature for one hour to remove the binder, followed by heating to the desired sintering temperature of 1220^0C. Only the sintering time was varied between 30 to 120 minutes.

After sintering, density of the samples were measured and then compared to the theoretical density to express the density in terms of percent theoretical density. Micro-structural analysis was performed using scanning electron microscope (SEM).

3. RESULTS AND DISCUSSIONS

(Table 1) shows the variation of % theoretical density and grain size with the variation of the sintering conditions; (Fig 1.) shows the variation of % theoretical density with the increase of sintering time and (Fig 2.) shows the variation of grain size with the increase of sintering time. (Fig 3.) Shows the SEM micrograph of samples sintered at a fixed temperature of 1220^0C where the sintering time was gradually increased from 30-120 minutes.

From the % theoretical density vs sintering time curve (Fig 1.); three stages of densification were identified followed by a stage of dedensification, based on the rate of densification. In the 1st stage, densification occurs by both atomic diffusion and grain boundary diffusion. Since diffusion is an energy related phenomenon and in the 1st stage, energy was available in the form of both heat and induced stress on the particles during pressing; the overall diffusion process was really fast, which resulted in a very high rate of densification.

Table 1: Variation of % theoretical density and grain size at different sintering times

Sintering temperature (^{0}C)	Sintering time (Minutes)	%Theoretical density	Grain size (μm)
1220	30	84.3	0.70
1220	40	86.8	1.40
1220	50	88.0	4.15
1220	60	89.0	5.50
1220	70	89.5	6.60
1220	80	90.0	9.00
1220	90	90.2	9.60
1220	100	90.3	10.2
1220	110	90.2	11.0
1220	120	89.7	13.0

In the 2nd stage, densification rate slowed down. From equation (1), it can be seen that, with increase in sintering time, neck area between grains starts to increase. During this process, the centers of the grains come close together and merge to form large grains. From, equation (2), it can be seen that with increasing grain size, rate of densification starts to decrease. This is clearly seen from (Fig 1-2). In the 3rd stage, grain boundary migration becomes very fast. As a result, the porosities get isolated within the grains. In this situation, pore removal is possible only by atomic diffusion, which causes the rate of densification to become really low. For this reason, the % theoretical density remained almost constant in the 3rd stage. In the 4rth stage, the particles in the atomic level come so close to each other that a situation is reached, where they start to repulse each other. This results in a negative densification rate and lowering of the final density. This phenomenon is known as dedensification. Because of this dedensification phenomenon, the % theoretical density was lowered in the fourth stage. Although during sintering the rate of densification showed a particular pattern, the rate of grain growth showed an irregular pattern, but with increase in sintering time, the grain size continued to increase (Fig 2-3).

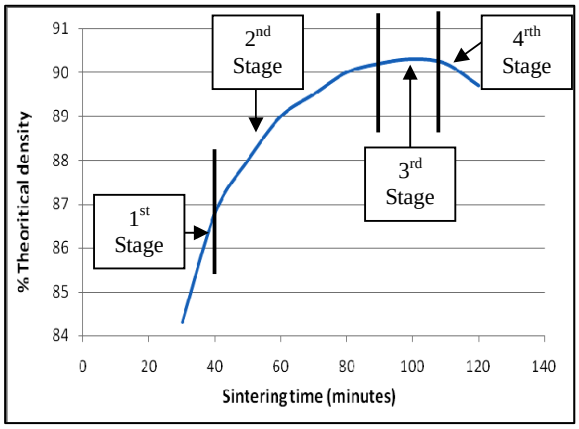


Fig 1. % Theoretical density vs sintering time curve

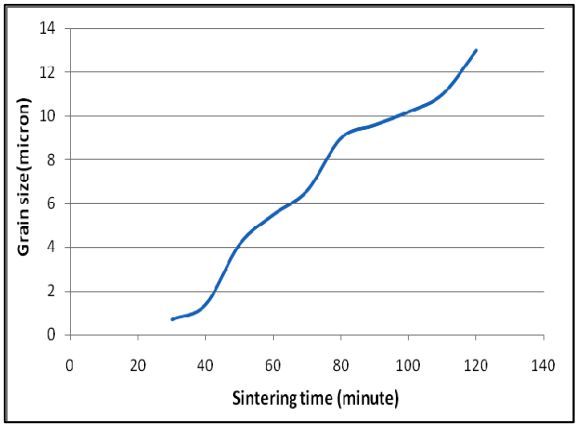
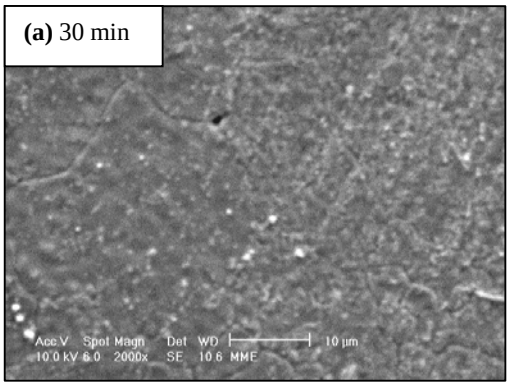
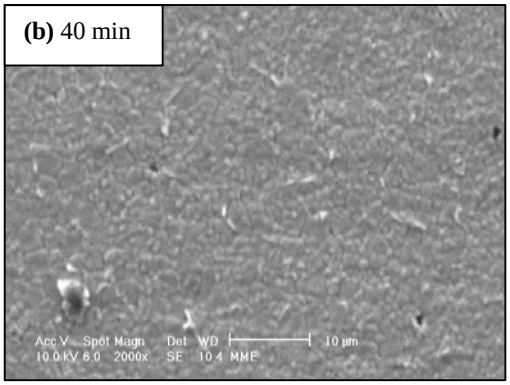


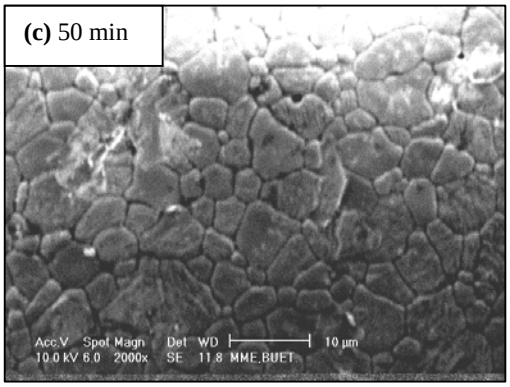
Fig 2. Grain size vs sintering time curve



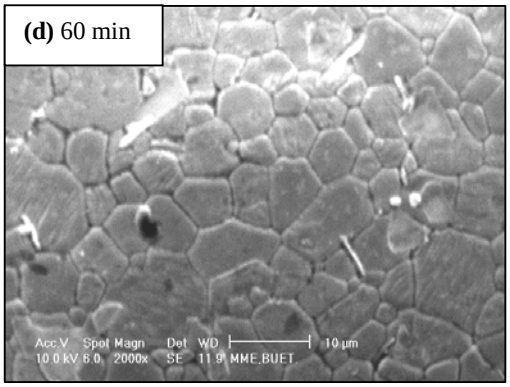
(a) 30 min



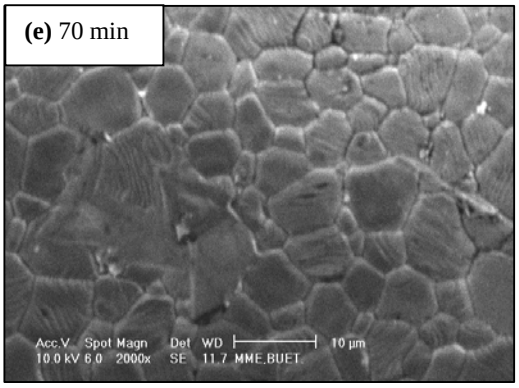
(b) 40 min



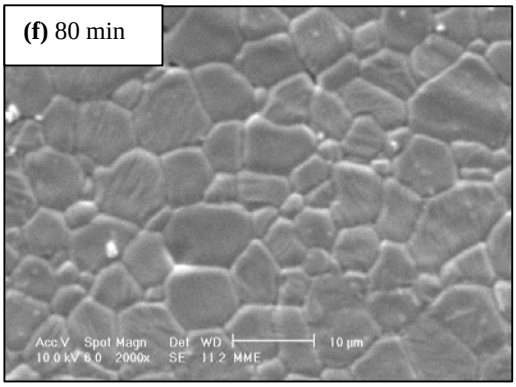
(c) 50 min



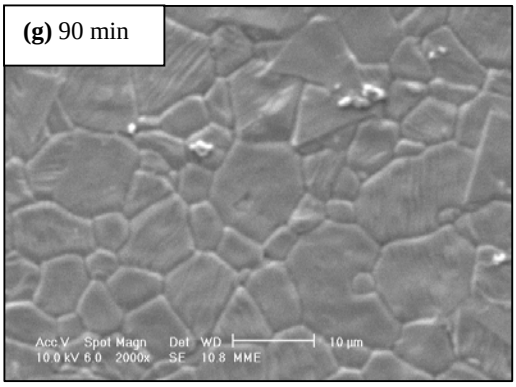
(d) 60 min



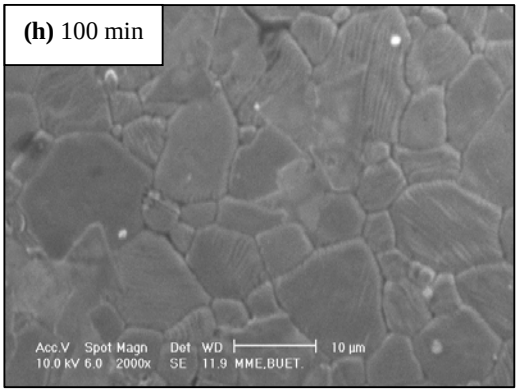
(e) 70 min



(f) 80 min



(g) 90 min



(h) 100 min

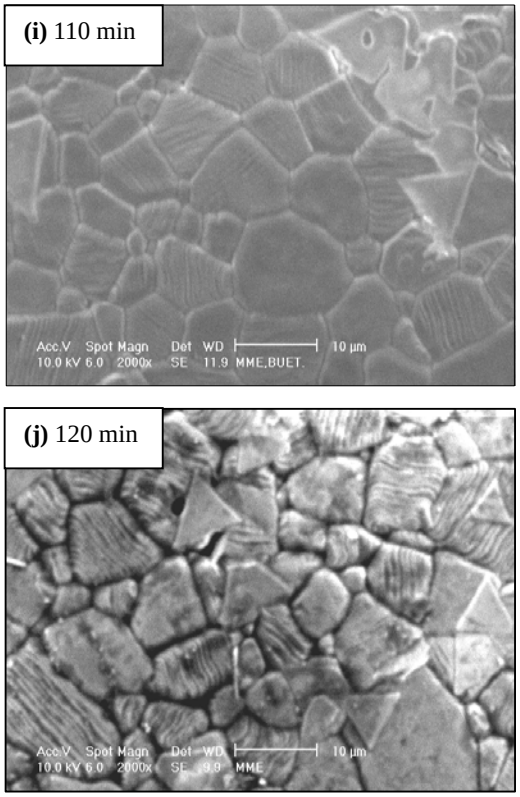


Fig 3. SEM micrograph of pure $BaTiO_3$ sintered at 1220^0C for sintering time ranging from 30-120 minutes (a-j)

4. CONCLUSION

When pure $BaTiO_3$ is sintered at a fixed temperature, with increase in sintering time both density and grain size increases. Three densification stages were identified followed by a stage of dedensification due to atomic repulsion of the particles. So the critical sintering time is up to the third stage of densification. In fact, the first two stages provide effective densification. Beyond the 2^{nd} stage, if the desired density is not achieved then densification should be carried out at higher temperature for shorter period of time.

ACKNOWLEDGEMENTS

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