JOURNAL OF MATERIALS SCIENCE 23 (1988) 3889-3893

The effect of sintering conditions on the grain growth of the $BaTiO_3$-based GBBL capacitors

BI-SHIOU CHIOU, SIN-TAH LIN
Institute of Electronics, National Chiao Tung University, Hsinchu, Taiwan
JENQ-GONG DUH
Department of Materials Science and Engineering, National Tsing Hua University, Hsinchu, Taiwan

$BaTiO_3$-based grain-boundary barrier layer capacitors are prepared by a conventional ceramic fabrication process with SiO_2, Dy_2O_3 and Nb_2O_5 dopants. A two-stage sintering process is employed to investigate the influence of the sintering conditions on the grain size of the $BaTiO_3$ ceramics. The reducing sintering atmosphere or reducing catalytic dopant decreases the apparent eutectic temperature of the $BaTiO_3$ ceramics. The decrease in the eutectic temperature associated with abnormal grain growth is related to the oxygen partial pressure during sintering. By properly employing the sintering temperature profile and the sintering atmosphere, a desirable microstructure with controlled grain growth could be achieved.

1. Introduction

Ferroelectric barium titanate has been extensively used as capacitor material. In particular, polycrystalline $BaTiO_3$ has been employed as the main ingredient to form a grain-boundary barrier layer (GBBL) capacitor [1] which is composed of a semiconductive grain and an insulative grain boundary. To obtain a high-performance GBBL capacitor [2, 3], the conductivity of the semiconductive grain, and also the resistivity of grain boundary should be as high as possible, but with an acceptable permittivity. The effective dielectric constant, ε_{eff}, of a GBBL capacitor is $\varepsilon_i(d_g/d_i)$, where d_g is the grain size, and d_i and ε_i are the thickness and dielectric constant of the insulative layer, respectively. Hence the larger the grain size, the larger the effective dielectric constant.

From the phase diagram of the BaO–TiO_2 system [4], it is found that a eutectic temperature exists at 1322° C for 49.5 mol % BaO–50.5 mol % TiO_2. Because the temperature is higher than 1322° C, there will be some extent of liquid phase present to promote the sintering. Proper control of the sintering conditions is thus expected to yield a rather uniform microstructure with the desired grain growth. Mostaghaci and Brook [5] proposed that there existed two grain-growth mechanisms: lattice diffusion-controlled processes and grain-boundary diffusion-controlled processes. The former would dominate the sintering process at higher firing temperatures, while the latter dominates at lower firing temperatures. Recently Chiou *et al.* [6] applied a controlled firing profile in the sintering of $BaTiO_3$ ceramics, and found that grain-boundary diffusion-controlled process induced an abnormal grain growth for specimens soaked at 1200° C for 10 min. For the $BaTiO_3$-based ceramics, the material purity, amount and type of dopant, processing conditions, firing and cooling temperature profiles, and sintering atmosphere, all affect the microstructure and thereafter the electrical properties of the capacitors. The purpose of this study was to employ two-stage sintering to investigate the influence of sintering conditions on the microstructure of the GBBL capacitors.

2. Experimental procedure

$BaTiO_3$-based GBBL capacitors were prepared by a conventional ceramic fabrication process. The compositions employed in this study are given in Table I. Appropriate amounts of $BaCO_3$, TiO_2, SiO_2, Dy_2O_3, and Nb_2O_5 (reagent grade, Merck, Darmstadt, FRG) were mixed and wet milled in alcohol for about 24 h. The mixture was dried and crushed to break down any lumps formed during drying, and then calcined at 1100° C for 2 h. After recrushing, the powder was milled and cold pressed at a pressure of 78 MPa into discs 10 mm diameter and 1.5 mm thick. The pellets were sintered in two different atmospheres: CO/CO_2, and air. The CO/CO_2 atmosphere was provided by the oxidation of graphite inside a covered crucible. Specimens were fired with a two-stage sintering process, i.e. samples were first soaked at a temperature between 1220 and 1350° C for 1 h, and then fired at 1350° C for another hour. Microstructures of these samples were examined with a optical microscope (OM) to investigate the effect of soaking temperature during first-stage firing.

3. Results and discussion

For the two-stage sintering employed in this study, the soaking temperatures of the first stage were 1220, 1240, 1260, 1280, 1300, 1325, and 1350° C, while the second-stage temperature was fixed at 1350° C. If the firing temperature of the first stage was close to eutectic point, exaggerated abnormal grain growth may

0022-2461/88 $03.00 + .12

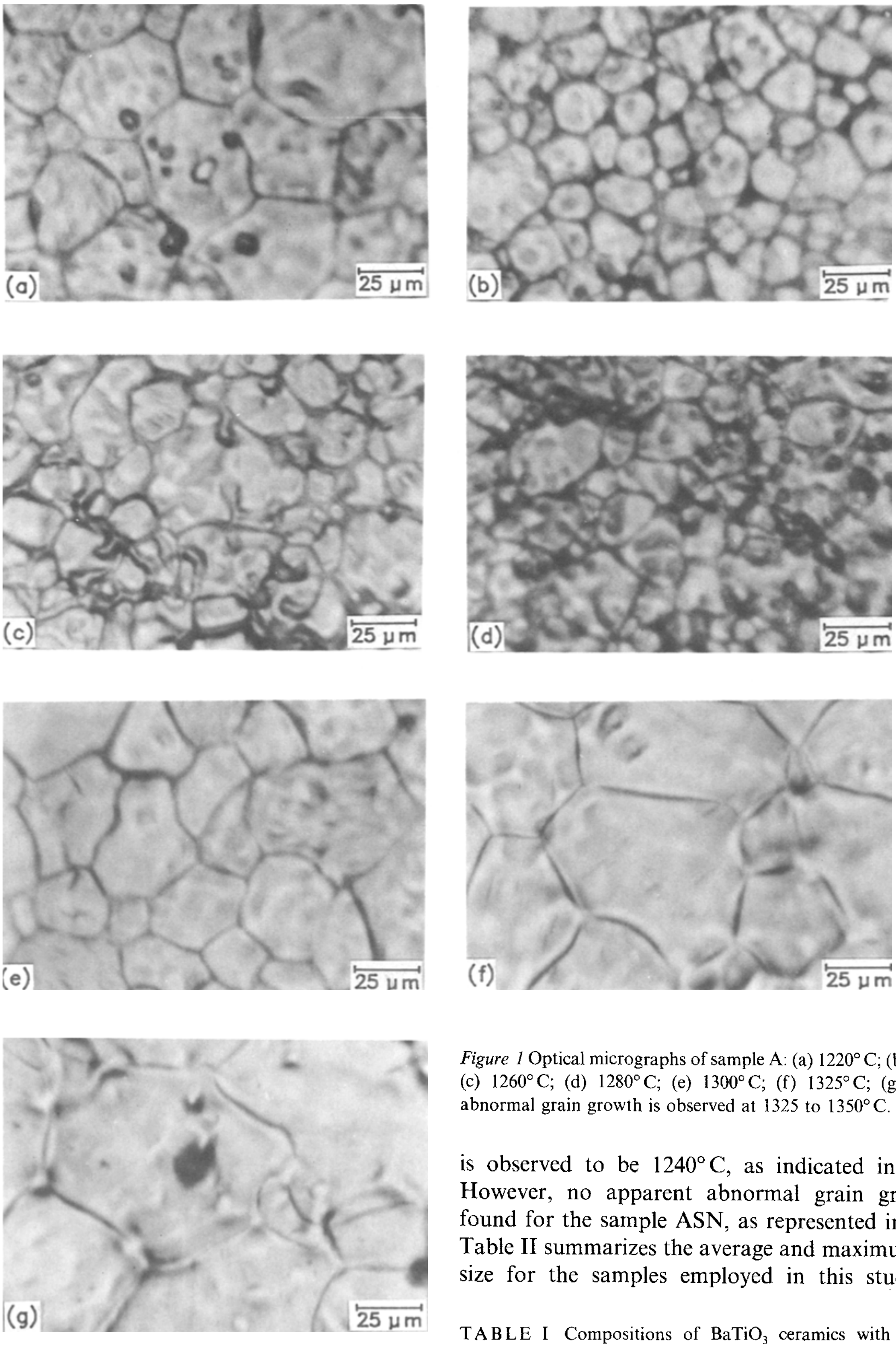


Figure 1 Optical micrographs of sample A: (a) 1220° C; (b) 1240° C; (c) 1260° C; (d) 1280° C; (e) 1300° C; (f) 1325° C; (g) 1350° C; abnormal grain growth is observed at 1325 to 1350° C.

occur [7], because there is insufficient liquid phase to wet all the grains. The grains adjacent to the liquid phase grow faster via grain-boundary diffusion enhanced by the liquid phase. At higher sintering temperatures, i.e. the second-stage firing, the grain grows via the lattice diffusion processes and a more uniform grain size can be expected. Fig. 1 shows the optical micrographs for sample A, undoped $BaTiO_3$, sintered in air. The exaggerated abnormal grain growth occurs when the first soaking temperature is around 1325 to 1350° C. The temperature at which the exaggerated grain growth takes place for sample AG is observed to be 1240° C, as indicated in Fig. 2. However, no apparent abnormal grain growth is found for the sample ASN, as represented in Fig. 3. Table II summarizes the average and maximum grain size for the samples employed in this study. The

TABLE I Compositions of $BaTiO_3$ ceramics with two-stage sintering process

Sample	Composition (mol %)					Sintering atmosphere
	$BaTiO_3$*	SiO_2	Dy_2O_3	Nb_2O_5	Graphite	
AG	99	0	0	0	1	Air
A	100	0	0	0	0	Air
ASD	98.9	1	0.1	0	0	Air
ASDN	98.85	1	0.1	0.05	0	Air
ASN	98.9	1	0	0.1	0	Air
CG	99	0	0	0	1	CO/CO_2
C	100	0	0	0	0	CO/CO_2
CSD	98.9	1	0.1	0	0	CO/CO_2
CSDN	98.85	1	0.1	0.05	0	CO/CO_2
CSN	98.9	1	0	0.1	0	CO/CO_2

*Ti/Ba = 1.01 for liquid-phase sintering.

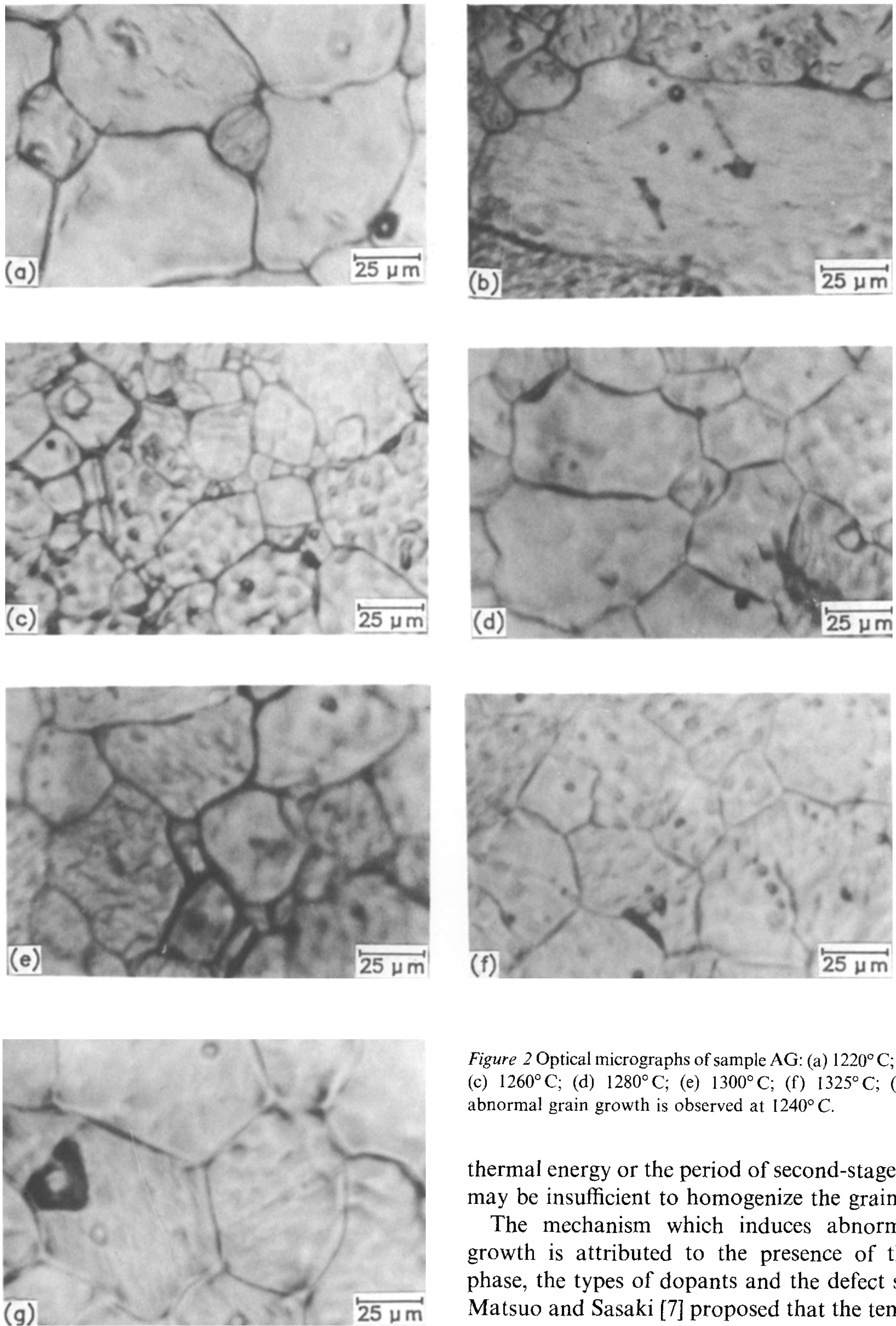
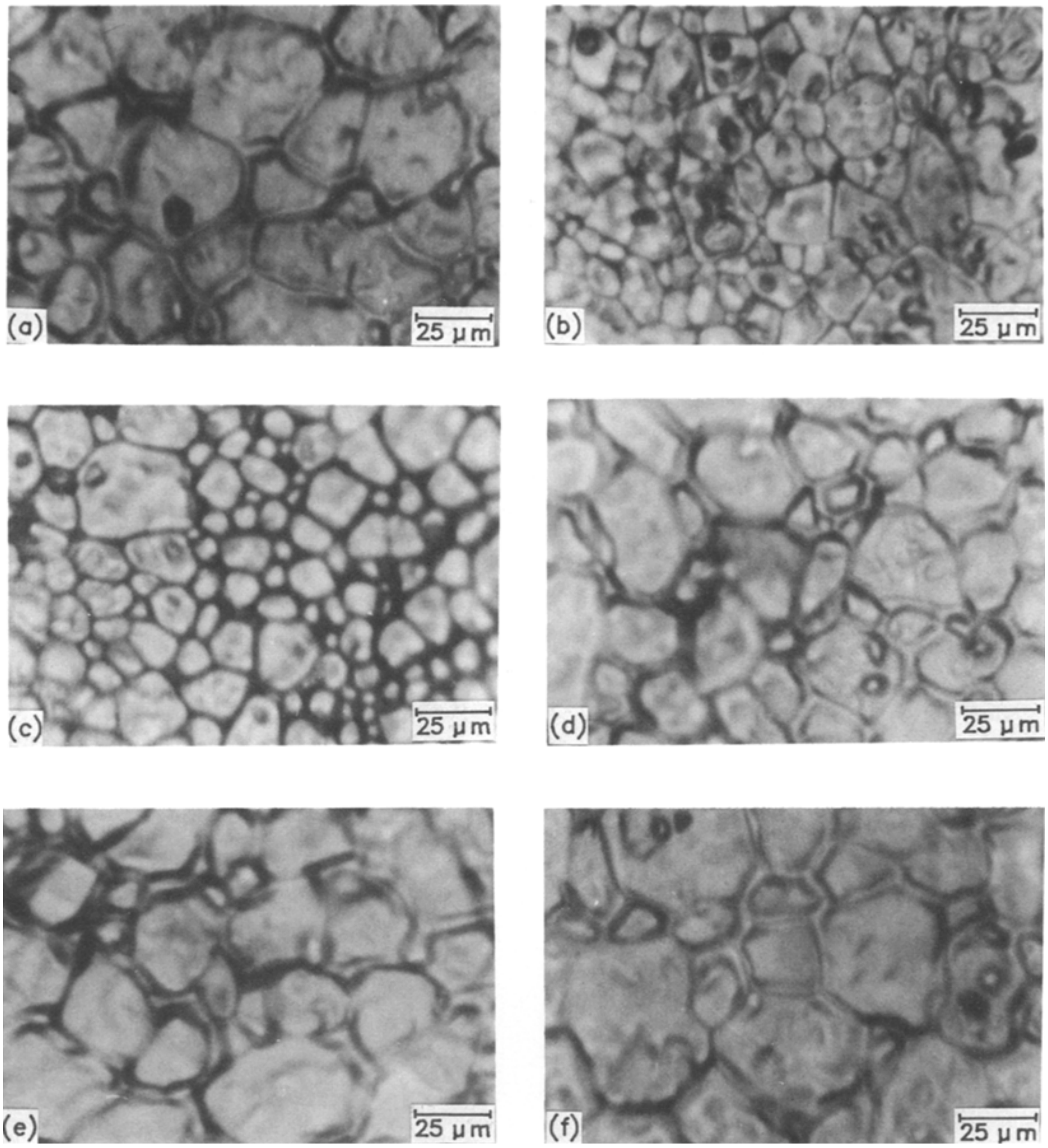


Figure 2 Optical micrographs of sample AG: (a) 1220° C; (b) 1240° C; (c) 1260° C; (d) 1280° C; (e) 1300° C; (f) 1325° C; (g) 1350° C; abnormal grain growth is observed at 1240° C.

average grain size is estimated by the intercept method on the basis of the optical micrograph. From Table II, it is seen that there are in total four samples exhibiting exaggerated abnormal grain growth after the two-stage sintering. In addition to samples A and AG as indicated in Figs 1 and 2, samples C and CSN also exhibit abnormal growth at the first soaking temperature around 1260° C and 1240 to 1260° C, respectively. It is believed that the sintering mechanism during the first-stage soaking process causes the grain to grow. Nevertheless, during the second-stage soaking process it can not make the grain uniformly distributed, as the thermal energy or the period of second-stage sintering may be insufficient to homogenize the grain.

The mechanism which induces abnormal grain growth is attributed to the presence of the liquid phase, the types of dopants and the defect structure. Matsuo and Sasaki [7] proposed that the temperature promoting abnormal grain growth would represent the eutectic temperature of associated specimen. The eutectic point of sample A, i.e. the undoped $BaTiO_3$ sintered in air, is about 1325 to 1350° C, which is comparable to the eutectic temperature, 1322° C, in the BaO–TiO_2 phase diagram. For sample C, the undoped $BaTiO_3$ sintered in CO/CO_2, the first soaking temperature with abnormal grain growth corresponds to 1260° C, which indicates that the apparent eutectic temperature occurs at 1260° C. As compared to sample A, this implies that the reducing sintering atmosphere, CO/CO_2, could decrease the eutectic temperature from 1322° C down to 1260° C. For sample AG, the $BaTiO_3$ doped with 1 mol % graphite, the apparent eutectic temperature is observed around



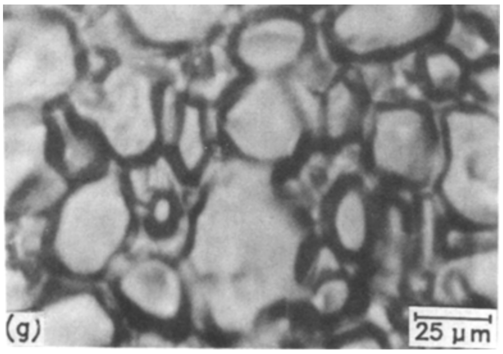


Figure 3 Optical micrographs of sample ASN: (a) 1220° C; (b) 1240° C; (c) 1260° C; (d) 1280° C; (e) 1300° C; (f) 1325° C; (g) 1350° C; no abnormal grain growth is visible.

1240° C, as obtained from Table II. This indicates that the graphite acts as a reducing agent, which is comparable to the CO/CO_2 reducing atmosphere. In addition, sample CSN, i.e. $BaTiO_3$ with 0.1 mol % Nb_2O_5 and 1 mol % SiO_2 sintered in the CO/CO_2 atmosphere, also represents a decreased eutectic temperature at 1240 to 1260° C. It appears that other samples without abnormal grain growth may have eutectic points out of the range 1240 to 1350° C.

Dopant ions can be introduced into the barium titanate lattice either during calcination at temperatures where the formation of $BaTiO_3$ takes place or by grain growth during sintering of $BaTiO_3$. Because the bulk diffusion of dopants is very slow, grain growth is found to be an effective way of incorporating dopant into the $BaTiO_3$ lattice. However, incorporation of larger amounts of dopants into the perovskite lattice is limited, as high concentrations of dopant in the reacting mixture hinder grain growth. Recently, Drofenik and coworkers [8–10] reported that during sintering of donor-doped $BaTiO_3$ in the presence of TiO_2/SiO_2-rich liquid phase, oxygen associated with the grain-growth process would be released. In heavily doped samples, the partial pressure of oxygen has a pronounced influence on the sintering and accompanying phenomena. Grain growth with the simultaneous incorporation of dopant atoms into the $BaTiO_3$ lattice requires the release of oxygen from the reaction mixture. Consequently, low oxygen partial pressure favours grain growth. On the other hand, a high oxygen partial pressure hinders the process. Hence, the sintering atmosphere also has a predominant effect on the grain size of the $BaTiO_3$ ceramics. On the

TABLE II Grain sizes of two-stage sintered $BaTiO_3$ ceramics

Sample designation	Grain size	1st stage soaking temperature (° C)						
		1220	1240	1260	1280	1300	1325	1350
AG	av.	40	40	20	30	30	30	30
	max.	60	> 100*	50	50	50	50	50
A	av.	20	15	15	15	20	30	50
	max.	40	25	25	25	40	60*	80*
ASD	av.	15	15	15	18	18	18	18
	max.	25	25	25	30	30	30	30
ASDN	av.	< 10	$\leqslant 10$	$\leqslant 10$	$\leqslant 10$	$\leqslant 10$	$\leqslant 10$	< 10
	max.	20	< 10	20	30	25	40	45
ASN	av.	18	12	8	15	18	18	18
	max.	30	25	25	25	30	30	30
CG	av.	10	10	10	10	10	10	10
	max.	25	25	20	20	20	20	20
C	av.	15	10	> 50	10	< 10	$\leqslant 10$	8
	max.	25	25	> 100*	25	25	< 10	10
CSD	av.	8	8	8	8	8	8	8
	max.	20	20	20	20	20	20	25
CSDN	av.	15	15	10	10	10	10	10
	max.	35	35	25	25	20	20	20
CSN	av.		45	45	20	15	15	15
	max.		> 100*	> 100*	40	25	25	30

*Exaggerated abnormal grain growth.

basis of the thermodynamic calculation [11], the oxygen partial pressure with the CO/CO_2 atmosphere employed in this study is fairly small compared to that for the air sintering. The relatively low oxygen partial pressure associated with sample C thus induces an enhanced degree of grain growth, which alternatively reduces the apparent eutectic temperature to 1260° C, compared to 1325° C for sample A sintered in air.

4. Conclusion

Two-stage sintering is employed to investigate the influence of the sintering conditions on the grain size of the $BaTiO_3$ ceramics. The reducing sintering atmosphere or reducing catalytic dopant decreases the apparent eutectic temperature of the $BaTiO_3$ ceramics. The temperature associated with abnormal grain growth for $BaTiO_3$ sintered in CO/CO_2 atmosphere is decreased to around 1260° C compared to 1325° C for the specimen sintered in air. The decrease in the eutectic temperature for abnormal grain growth is appreciated with the influential partial pressure of oxygen associated with the sintering conditions. Low oxygen partial pressure favours grain growth and also the incorporation of dopants into the $BaTiO_3$ lattice. By properly employing the sintering temperature profile and the sintering atmosphere, a desired microstructure with controlled grain growth could be obtained.

References

1. G. GOODMAN, in "Grain Boundary Phenomena in Electronic Ceramics", Advances in Ceramics, Vol. 1, edited by L. M. Levinson (The American Ceramic Society, Columbus, Ohio, 1981) p. 215.
2. S. WAKU, *Rev. Electr. Commun. Lab.* **15** (1967) 689.
3. J. P. BONSACK, *Amer. Ceram. Soc. Bull.* **50** (1971) 488.
4. E. M. LEVIN, C. R. ROBBINS, H. F. McMURDIE and M. K. RESER (eds), in "Phase Diagram for Ceramists" (The American Ceramic Society, Columbus, Ohio, 1964) p. 98.
5. H. MOSTAGHACI and R. J. BROOK, *Trans. J. Brit. Ceram.* **82** (5) (1983) 167.
6. B. S. CHIOU, C. M. KOH and J. G. DUH, *J. Mater. Sci.* **22** (1987) 3893.
7. Y. MATSUO and H. SASAKI, *J. Amer. Ceram. Soc.* **54** (1971) 471.
8. M. DROFENIK, A. POPORIC and D. KOLAR, *Amer. Ceram. Soc. Bull.* **63** (1984) 702.
9. M. DROFENIK, A. POPORIC, L. IRMANCNIK, D. KOLAR and V. KRASEVECM, *J. Amer. Ceram. Soc.* **65** (1982) C-203.
10. M. H. DROFENIK, *ibid.* **69** (1986) C-8.
11. D. R. GASKELL, in "Introduction to Metallurgical Thermodynamics" (Hemisphere, New York, 1981) p. 241.

Received 8 September 1987
and accepted 1 March 1988