ACTA STEREOL 1994; 13/2: 381-388
PROC 6ECS PRAGUE, 1993
ORIGINAL SCIENTIFIC PAPER

EFFECTS OF SINTERING TIME AND TEMPERATURE ON $BaTiO_3$ - CERAMIC MICROSTRUCTURAL CHARACTERISTICS

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ABSTRACT

The effects of time and temperature of sintering on microstructural characteristics of barium-titanate were investigated in this paper. Microstructural investigation have been done by optical microscopy using quantitative analysis methods and SEM microscopy. The specimens were prepared from high purity $BaTiO_3$ powders with 0.10% CeO_2 and 0.14% $MnCO_3$, and sintered at various temperatures ranged from 1190 °C to 1370 °C, for different times. All the samples were examined by quantitative microstructural analysis and parameters related to the grain size and porosity have been determined such as: section area (A), perimeter (L_P), form factor (f), numerical density (N_A) and volume fraction (V_v) of pores.

The results have shown that the grain sizes increase with the increase of sintering temperature, but with different intensity depending on time of sintering. For two different times of sintering, the critical sintering temperature has been determined.

During the process of sintering although the pore sizes increase, the reduction on N_A and V_v occurred. The reduction of L_P parameter value and the growth of f parameter pointed out the agglomeration of pores as the sintering temperatures are raised.

The mathematical modelling method has been used to discuss the experimental results. A cumulative density function is proposed for interpretation of the results obtained in this study. A great extent of agreement between theoretical and experimental results pointed out the beneficial use of this method in microstructural investigation of ceramic materials.

Key words: ceramics, grain size distribution, microstructure, sintering process.

INTRODUCTION

Advanced applications of ceramic systems considering that they give wide possibilities of application in electronics for their electrical, dielectric and ferroelectric characteristics deserve a special scientific and technological interest. Characteristics of barium titanate such as high positive temperature coefficient of resistivity (PTCR effect), a great dependence of electrical resistivity on voltage (varistor's effect), superconduction behaviour and others, make possible development of a great

number of different types of electronic components (Semiconducting Barium Titanate, 1977; Mader at al., 1987). Optimization of corresponding properties of $BaTiO_3$ - ceramic systems, depends on understanding the relation between structure and related properties, and seems to be a new qualitative step in processing of these ceramic materials (Kahn, 1971; DeHoff, 1989; Mitić, 1989).

The properties of barium-titanate systems present a complex function of a great numbers of parameters of structure and of ferroelectric characteristics of system. Therefore the designing and processing of $BaTiO_3$ is lead down on to the definition of dynamic system with recurrent coupling that optimizes the structure of $BaTiO_3$. The complexity of the investigation of these systems resulting from the fact that the polycrystalline system obtained by the sintering process is in question.

A various dopants could be used to improve the particular properties of barium-titanate. It has been well known that the dopants and sintering conditions significantly influence the densification and grain growth of ceramic materials. Therefore it can be said that all these parameters make a phenomenon of mutual relations and only their complete understanding and control may contribute to the optimization of $BaTiO_3$ - ceramic characteristics. The optimization of microstructural characteristics was the main aim of this study.

EXPERIMENTAL

The basic starting material for this study was Murata barium-titanate powder of high purity, with the additives of 0.10% CeO_2 and 0.14% $MnCO_3$. The powder particles were of spherical form, and the agglomerates sizes ranged from 10 μm to 120 μm. The special attention was paid on the pressing and sintering conditions. The density of pressed samples was $3.4 \cdot 10^3$ kg/m^3 and for easier separation after sintering, the samples were covered by special fireproof powder. Sintering has been done in a tunnel furnace type "CT-10 MURATA" at 1190, 1240, 1290 and 1370 °C. The heat treatment procedure has been done so that each series of samples entered the furnace with a characteristic passing time, 40 and 60 minutes which corresponds to two and three hours of sintering at given temperature.

All the specimens were examined by optical and SEM microscopy followed by quantitative analysis method. By this method the size and shape of grains and pores as well as the number of grains and pores could be obtained.

The grain size measuring was determined by linear method of intercept length (l) (DeHoff, 1987). A large number of samples included in this study assumed a reliable statistical data on the following parameters: perimeter (L_P), the section area (A), maximum diameter (D_{max}) of pores and volume fraction (V_V) of pores have been determined. Consequently the form factor of perimeter (f) and the density (pore number per μm^2, N_A) were determined as well. The obtained statistical results of minimum, maximum and mean parameters values are given in Tbl 1.

RESULTS AND DISCUSSION

The effects of the sintering time and temperature influence on the grain size l, have been investigated through linear method of segments measurements. It has been observed that the observed values of grain sizes were in the range up to the 22 μm, and could be classified in to the classes with the width of the class of 1,5 μm. The corresponding values of absolute frequencies for different sintering times and different sintering

Table 1. Characteristic values for grains and pores parameters in function on sintering conditions.

Sintering conditions		Grain size (l) (μm)			A(μm^2)			Lp(μm)			Dmax(μm)			f			$N_A \cdot 10^{-3}$	Vv(%)
		min.	max.	mean	min.	max.	mean	min.	max.	mean	min.	max.	mean	min.	max.	mean	(μm^{-2})	
1190°C	40'	0.47	8.72	2.3	0.06	44	11.4	6	33.6	14	2.5	12.2	4.6	0.02	1	0.73	6.5	7.38
	60'	0.94	12	3.5	1.5	116	15.4	3.5	59	17.5	2	16.3	5.1	0.2	1	0.78	5.7	9.7
1240°C	40'	0.57	16.9	3.4	1.9	57.5	11.6	5.3	50.9	14	2.3	13.8	4.6	0.22	1	0.78	4.7	6.73
	60'	1.3	13.8	4.5	2.5	132	16.9	5.6	60	14.7	1.6	18.5	5.3	0.2	1	0.79	4.9	8.7
1290°C	40'	0.7	19	4.4	1.6	101	14.2	5	51	12.9	2	14	4.95	0.3	1	0.82	4.47	5.7
	60'	1.16	25.1	7.6	1.9	126	19	5	56	13.8	1.8	20	6	0.3	1	0.81	4.5	7.4
1370°C	40'	1.1	24	8.1	2.5	125	15.9	5.6	52	13.2	1.8	15.6	5.2	0.39	1	0.84	3.6	5.1
	60'	0.95	27	8.3	2.8	178	20	7.4	50	13.3	2.7	20	6.2	0.26	1	0.84	3.9	7

temperatures were given in Tbl. 2. By analysis of these frequencies a cumulative density function has been obtained in the following form:

$$F(l)=a\left\{1 - e^{-b\ (l\ -\ l^*)}\right\} \qquad (1)$$

where **a** and **b** are parameters, and l^* characteristic value of grain size $\{F(l=l^*) \equiv 0\}$. The function given by Eq. 1 fits very well the dependence of grain size on temperature and time of sintering. The results given in Tbl. 2 are graphically presented in Fig. 1a and Fig. 1b. The values of parameters **a**, **b** and l^* are given in Tbl 3. It could be noticed that at lower sintering temperatures of 1190 °C and 1240 °C typical grain sizes are inside narrower interval of values, so the critical size of grain size is about 10 μm, since there is no grain sizes greater from this critical value. For 1290 °C, the range of values is much more wider. For sintering temperature of 1370 °C the leveling of curve occurred for the grain sizes greater than 25 μm. This curve has a considerable less slope in relation to the previous ones. From Fig. 1b it could be seen that the longer sintering times bring about wider intervals of grain sizes at lower temperatures.

SEM microstructures given in Fig. 2 confirm that the grain size ($\bar{l}$) increases with temperature. Corresponding curves in Fig. 1a, clearly indicate the constant shift towards greater grain sizes. The significant grain growth begins above 1290 °C and is remarkable at 1370 °C.

The measurements of porosity given in Tbl. 1, show that pore volume fraction decreases as the temperature of sintering is raised with the simultaneous reducing of pore number per square area. The pore size, expressed as area A, and maximal diameter D_{max}, increase. At the same time parameter L_P decreases and form factor f increases approaching the value of 1 which is characteristic for a circle. That points out that pores take the symmetrical form with the increase of sintering temperature.

The results for the passing time of 60 minutes (3 hours of sintering) given in Tbl. 1 and in Fig. 1b and Fig. 2, reveal that the grains grow rapidly above 1290 °C. It could be noticed also, that the mean grain size for 60 minutes passing time, exceeds that obtained for 40 minutes passing time. The porosity is also changing with sintering temperature: values of V_V and N_A decrease and pore growth is observed.

As for 40 minutes passing time pores become spherical with form factor f close to 1, as the temperature is raised. The analysis of the grain size distributions for the same sintering temperature and different time indicated that the important difference exists at lower temperatures. The time of sintering at 1370 °C does not influence the grain size to a great extent.

CONCLUSION

On the basis of the results obtained in this study, it could be concluded that introduction of the mathematical method given by a cumulative density function, as is proposed, gives the opportunity to describe the possible distribution of grain sizes under the experimental limits.

The observed agreement, between experimental and theoretical results, pointed out that the described mathematical model could be used for a wider intervals of grain and pores sizes. Therefore, the effects of grain and pore size, as well as their distributions, on the properties of barium-titanate systems could be better understood.

Table 2. Grain size as a function of sintering temperature and sintering time.

Class			T(°C)							
			1190		1240		1290		1370	
	l(μm) From	to	t(min) 40	60	t(min) 40	60	t(min) 40	60	t(min) 40	60
1.	0	1.5	149	78	58	7	45	2	2	72
2.	1.5	3	209	179	186	104	132	36	41	51
3.	3	4.5	60	167	104	160	101	67	69	75
4.	4.5	6	24	52	48	94	74	82	83	89
5.	6	7.5	7	23	34	47	37	86	59	59
6.	7.5	9	1	7	9	17	25	52	38	48
7.	9.0	10.5		3	3	13	9	36	43	40
8.	10.5	12		1	6	5	12	26	30	31
9.	12	13,5			1	1	6	12	25	10
10.	13.5	15			0	2	2	18	17	18
11.	15	16,5			0		3	10	12	7
12.	16.5	18			1		3	11	10	5
13.	18	19.5					1	4	7	4
14.	19.5	21						4	7	3
15.	21	22.5							3	3

Table 3. The parameter's values of cumulative density function.

T(°C)	t(min)	a	b(1/μm)	l*(μm)
1190	40	100.2	0.72	0.1
	60	101.7	0.46	0.6
1240	40	100.2	0.40	0.1
	60	102.5	0.31	0.6
1290	40	100.5	0.28	0.1
	60	103.7	0.15	0.6
1370	40	101.2	0.16	1.2
	60	106.1	0.15	0.6

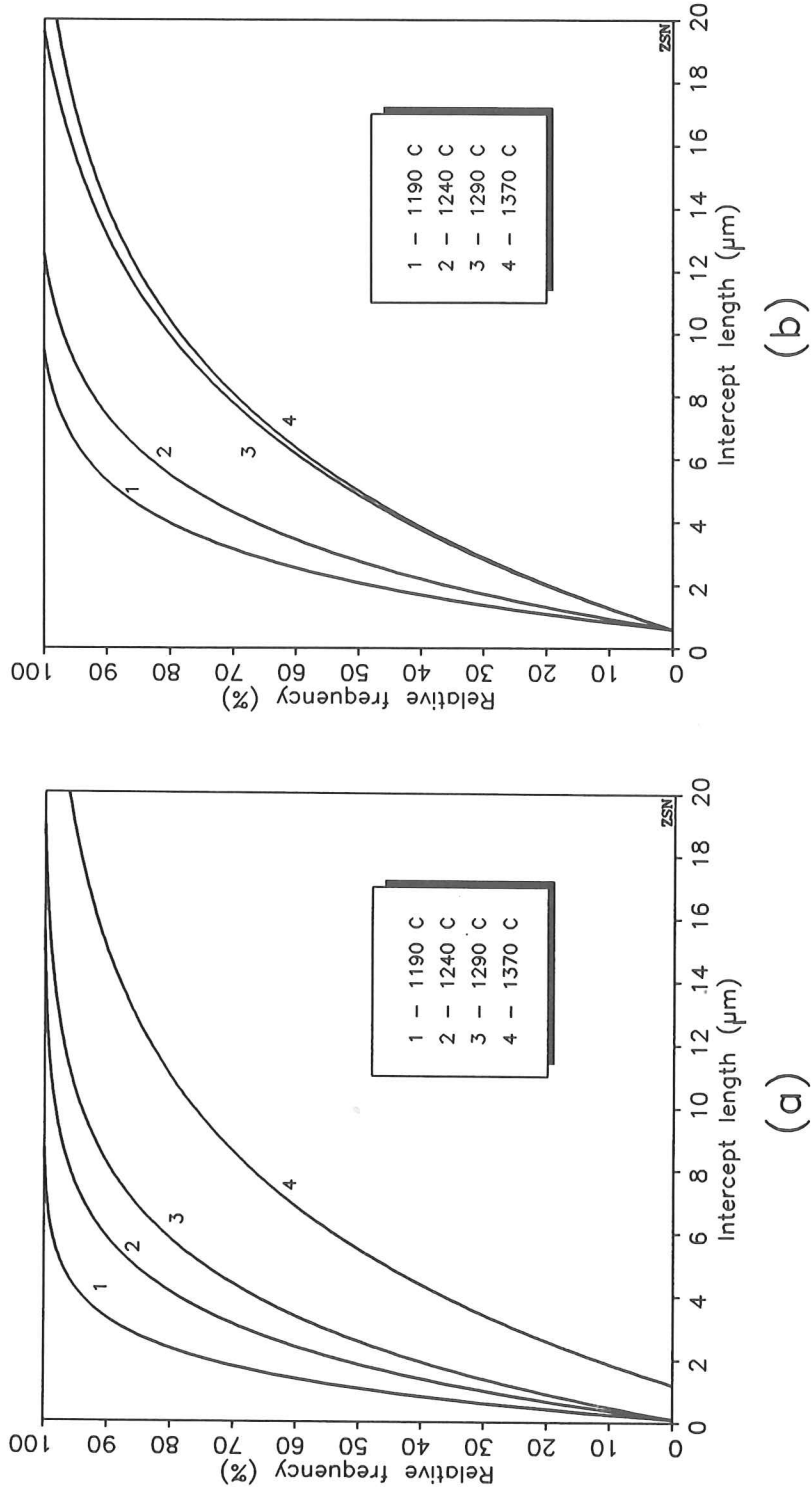

Fig.1 Calculated cumulative density functions for grain size distribution (a) passing time 40 min. (b) passing time 60 min.

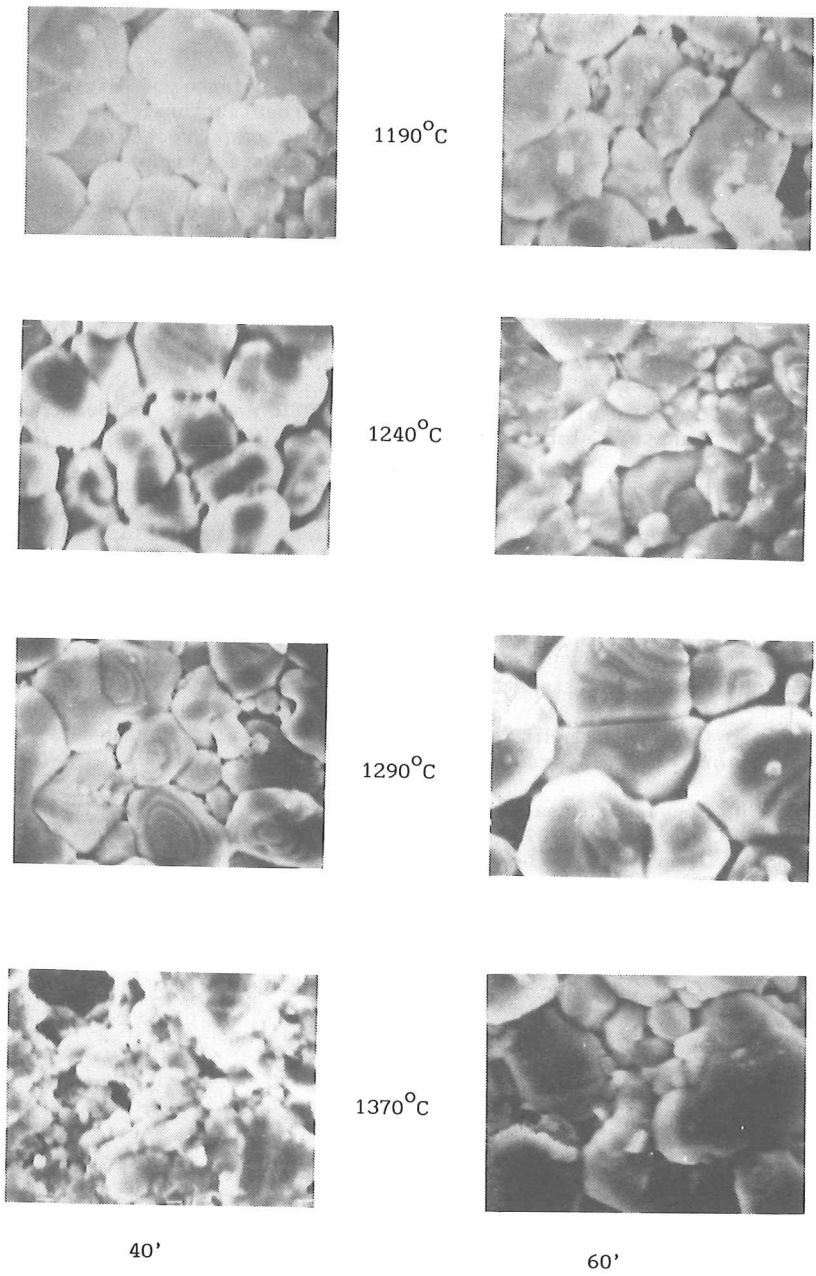

Fig.2 SEM microstructures of $BaTiO_3$ - ceramic samples (x5000).

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