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Subsolidus grain growth in donor doped barium titanate

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Grain growth in donor doped $BaTiO_3$ was studied below the temperature of liquid phase formation. It was found that a high donor concentration and high oxygen partial pressure effectively inhibit grain growth rate during sintering. Defect chemistry, derived from a model consistent with electrical measurements, well describes the grain growth properties of donor doped $BaTiO_3$ in the subsolidus grain growth region.

1. Introduction

One of the essential features of donor doped $BaTiO_3$ ceramics is the close relation between donor concentration, oxygen partial pressure and their microstructural properties, usually designated as the grain size anomaly, i.e. at a given donor dopant concentration and oxygen partial pressure the $BaTiO_3$ ceramic exhibits a dramatic decrease of electric conductivity, associated with the formation of a fine grained microstructure. A high donor concentration strongly retards the grain growth of donor doped $BaTiO_3$ when sintered in air or oxygen, leading to a high resistivity ceramic.

Though this phenomenon has been known for a long time and has often been the subject of intensive investigations, a fully satisfying explanation has still not been obtained. In the main, two approaches were formulated about this phenomenon. One is based on the persuasion that kinetic processes govern this effect [1–4], while the other is associated with the belief that this phenomenon is of thermodynamic origin [5].

In the first case defect chemistry derived from a model consistent with conductivity measurements is applied [6, 7]. However, in this case no liquid phase should be present on the grain boundary during sintering to interfere with the diffusion processes, and thereby the restoration of equilibrium of the defect concentration predicted by the model is applied. In the second case it is assumed that rapid anomalous grain growth and formation of a reduced form of donor doped $BaTiO_3$ are constrained by the energetic demand associated with oxygen release during incorporation of the critical amount of dopant [5]. Formation of reduced donor doped $BaTiO_3$ occurs within a few minutes [8, 9], and is related to the temperature at which the anomalous grain growth starts.

The aim of this work was to study the grain growth process in donor doped $BaTiO_3$ at temperatures below the eutectic point, i.e. below the temperature of liquid phase formation during the grain growth process. At these temperatures solid state diffusion governs the mass transport and thus the grain growth process.

A relatively slow grain growth rate in this case allows the restoration of equilibrium during grain growth. Under such conditions the system will be closer to a steady state, and the lattice defects which rule the grain growth process in donor doped $BaTiO_3$ can be elucidated.

2. Experimental procedure

Donor (La) doped $BaTiO_3$ was prepared by thermal decomposition of La-Ba-titanyl oxalate. The procedure used by Kiss *et al.* [10] was adopted during preparation of La-Ba-titanyl oxalate from $TiCl_4$, $BaCl_2$ and $La(CH_3COO)_3$. The stoichiometric ratio, as well as the amount of La, was checked by X-ray fluorescence analysis. All chemicals used [$BaCl_2$, $TiCl_4$ and $La(CH_3COO)_3$] were more than 99.5% pure.

Samples investigated contained 0.2, 0.3, 0.4, 0.5, 0.7 and 0.95 at % La_2O_3 and had a BaO/TiO_2 ratio < 1. The donor doped $BaTiO_3$ powder used during this work was obtained by the calcination of complex La-Ba-titanyl oxalate at 800 °C for 2 h. The X-ray diffraction pattern of the calcined powder showed only tetragonal $BaTiO_3$ diffraction lines. The specific surface of the submicron powder obtained was 11 $m^2\,g^{-1}$.

From these powders samples were pressed in the form of pellets with $\phi = 5$ mm, $h = 3$ mm. These samples were sintered at 1280 and 1240 °C for up to 20 h. The heating and cooling rates were 10 °C min^{-1} for all samples. Samples were sintered at different oxygen pressures; 0.02 (air), 0.3 and 0.5 MPa. Electrical measurements were performed on sintered samples with In-Ga electrodes rubbed on the surfaces of the pallets. A d.c. bias in the ohmic region (< 1.5 V) was employed for the resistivity measurements. The microstructure of sintered samples was examined using optical and electron microscopes. The average grain size was determined by measuring the average grain cross-section area, using a modular system for semi-automatic quantitative evaluation of images.

3. Results and discussion

Fig. 1 shows the average grain size and electrical resistivity dependence on the amount of donor dopant in $BaTiO_3$. The correlation exhibits the well known features identified during sintering of donor doped $BaTiO_3$ in the presence of a liquid phase [11]. Samples doped with 0.3 at % and less were of a bluish colour, with specific resistivities < 5 kΩ cm. The average grain size of these samples did not exceed about 4 µm. Fig. 2a shows the microstructure of a 0.2 at % doped sample. On the other hand, samples doped with more than 0.4 at % dopant exhibit a yellow colour and were highly resistive. The microstructure of samples doped at 0.5 at % and more consisted of small grains of an average grain size of about 1 µm. The typical inhibited grain growth microstructure of a 0.95 at % doped sample is shown in Fig. 2b. The 0.4 at % doped samples proved to be an exception. The microstructure of these samples shows large grains of about 100 µm embedded in a fine grained matrix of grains, with an average size of approximately 1 µm, Fig. 3a. It is believed that the anomalous grain growth in the studied samples occurs below the appearance of $BaTiO_3$–$Ba_6Ti_{17}O_{40}$ eutectic liquid, which forms in TiO_2 excess $BaTiO_3$ at about 1320 °C. The preparation procedure was chosen to avoid contamination with SiO_2 and Al_2O_3, which may lower the eutectic temperature. Exaggerated grain growth in $BaTiO_3$ at subsolidus temperatures has been repeatedly described [12, 13].

At relatively low donor concentrations below 0.4 at %, where the anomalous grain growth is not blocked, semiconducting doped $BaTiO_3$ is formed. However, when the donor concentration increases and the critical concentration is transgressed, the anomalous grain growth is blocked. The critical donor dopant concentration, C, which blocks the anomalous grain growth can be estimated by using the relation $C_D = K_{111} \times 6\, V/D = 0.39$ at % [5], where $K_{111} = 1.7 \times 10^{-9}$ g ion^{-1} cm^{-2}, $V = 38.3$ cm^3 mol^{-1} (mol volume of $BaTiO_3$) and $D = 1 \times 10^{-4}$ cm is the critical average grain size for the system considered (see Fig. 3b). The estimated value is in agreement with the experimental value 0.4 at %, see Figs 1 and 3b. Here it must be stressed that in the subsolidus range a higher oxygen partial pressure does not block the anomalous grain growth; as in the case of liquid phase sintering [14] where the liquid phase encloses the grains and prevents restoration of the chemical equilibrium, but primarily influences the grain growth kinetics. Inhibition of anomalous grain growth consequently allows the formation of a fine grained microstructure with high electric resistivity, as demonstrated by the 0.5 at % and higher doped samples, Table I.

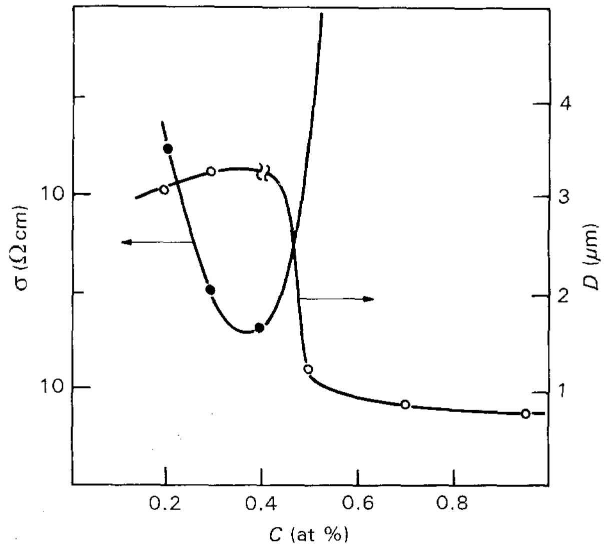

Figure 1 Average grain size and electrical resistivity of La doped $BaTiO_3$ samples sintered at 1280 °C for 20 h in air versus the dopant content: (○) 0.2 at %, (●) 0.4 at %.

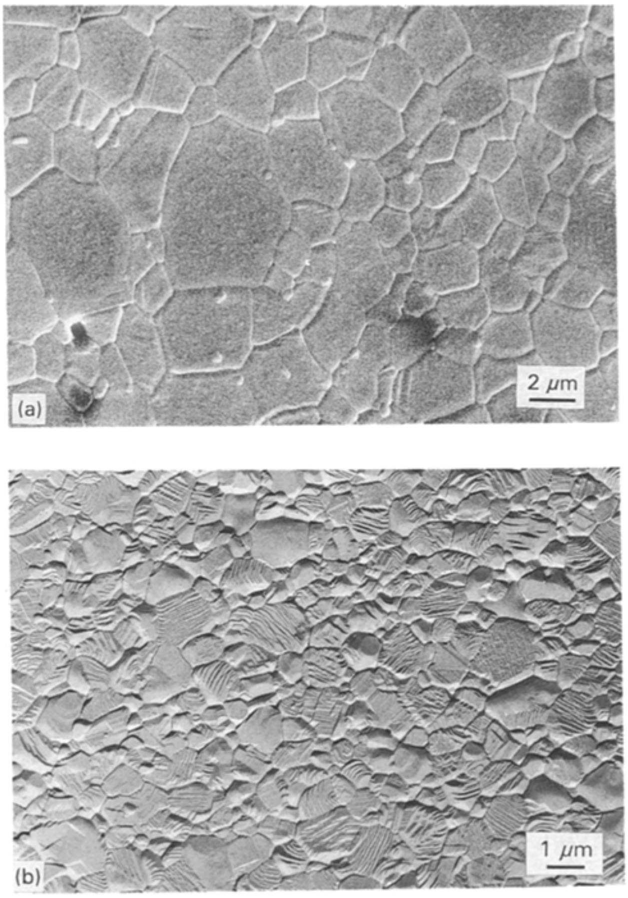

Figure 2 Microstructures of (a) 0.2 at % doped sample sintered at 1280 °C for 20 h in air, and (b) 0.95 at % doped sample sintered under the same conditions.

Between those two regions, i.e. semiconducting and insulating areas, an intermediate concentration range exists where only a few number of grains outgrow into the nuclei, which then continue to grow until they impinge upon each other. The basic grain growth mechanism was described as re-entrant angle assisted anomalous grain growth [12, 15]. The anomalous grains outgrow into a "skeleton" of semiconducting grains with overestimated grain size. When the sintering temperature was decreased to 1240 °C the

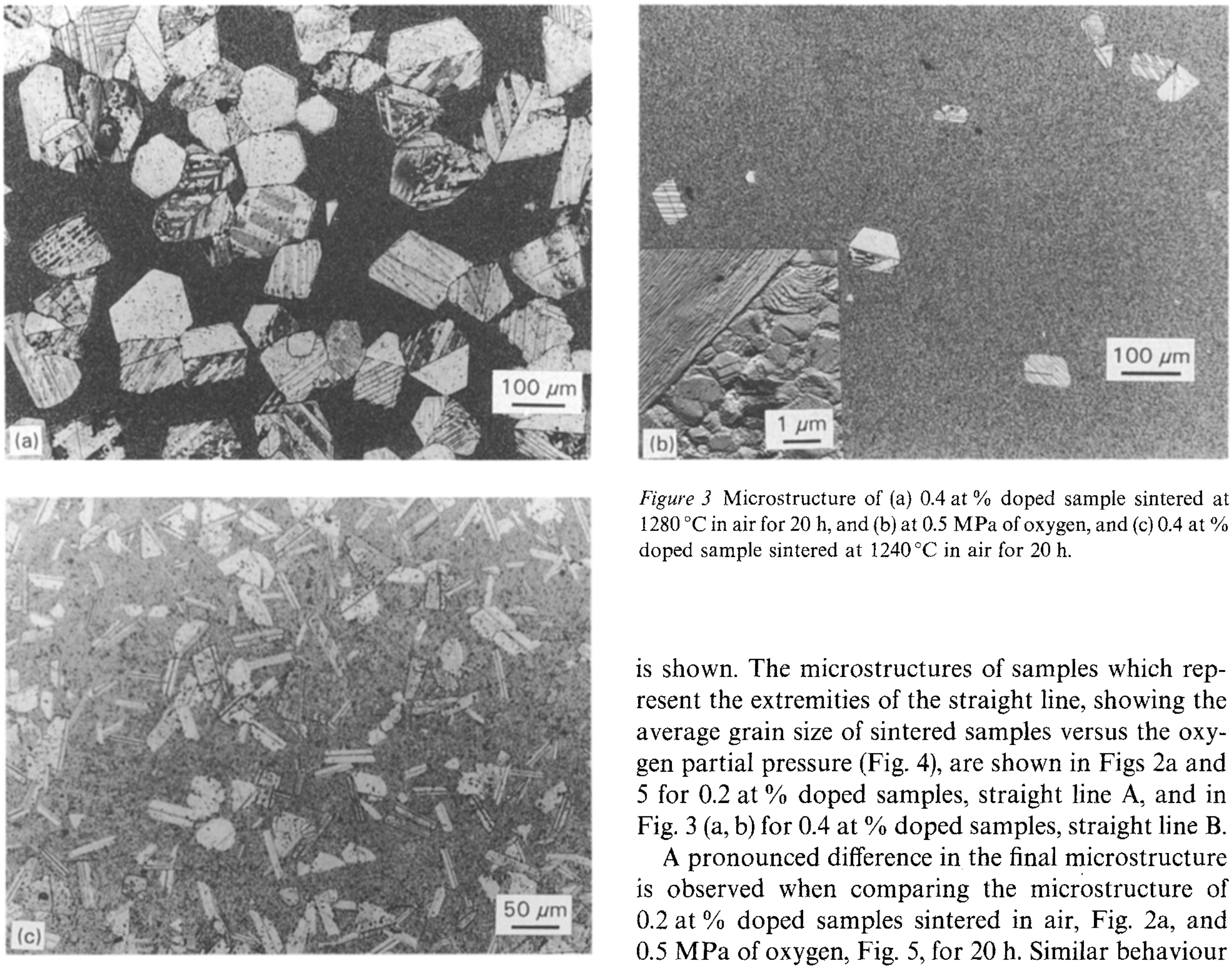

Figure 3 Microstructure of (a) 0.4 at % doped sample sintered at 1280 °C in air for 20 h, and (b) at 0.5 MPa of oxygen, and (c) 0.4 at % doped sample sintered at 1240 °C in air for 20 h.

TABLE I Microstructural or electrical properties of doped samples at 0.5 MPa

Composition (at % dopant)	Sintered at 1280 °C in air		Sintered under oxygen pressure	
	d (μm)[a]	R_{25} (Ω cm)	d (μm)	R_{25} (Ω cm)
0.2	3	2×10^3	< 2	$> 10^6$
0.3	3	5×10^2		
0.4[b]	–	3×10^2	–	$> 10^6$
0.5	< 1	$> 10^6$		
0.7	< 1	$> 10^6$		
0.95	< 1	$> 10^6$	< 1	$> 10^6$

[a] d, grain size diameter.
[b] Bimodal distribution.

anomalous grain growth in 0.4 at % doped samples could still be observed, Fig. 4c; however, the extent of growth is much less pronounced. These samples were highly ohmic.

Not only a high donor concentration, but also increased oxygen pressure influences the microstructure and electrical properties of the donor doped $BaTiO_3$ samples investigated. It has already been reported that a reducing atmosphere gives large grain size $BaTiO_3$ ceramics [16]. In Fig. 4 the average grain size versus the partial pressure of oxygen of 0.2 at % doped samples, labelled as curve A, and of anomalous grains in 0.4 at % doped samples, labelled as curve B, is shown. The microstructures of samples which represent the extremities of the straight line, showing the average grain size of sintered samples versus the oxygen partial pressure (Fig. 4), are shown in Figs 2a and 5 for 0.2 at % doped samples, straight line A, and in Fig. 3 (a, b) for 0.4 at % doped samples, straight line B.

A pronounced difference in the final microstructure is observed when comparing the microstructure of 0.2 at % doped samples sintered in air, Fig. 2a, and 0.5 MPa of oxygen, Fig. 5, for 20 h. Similar behaviour was observed when 0.4 at % doped samples were sintered in air and 0.5 MPa oxygen pressure. Anomalous grains in 0.4 at % doped samples grew at a slower rate if samples were sintered under higher oxygen pressure, and thus the number of grains which outgrew the average matrix grains was also smaller, as can be seen from Fig. 3a, b. On the other hand, the inhibited grain growth is associated with a drastic increase in electric resistivity. The electric resistivity, R, of sintered samples is presented in Table I.

From the results presented above it can be seen that the increase of oxygen partial pressure during sintering alters the microstructure and electric properties. A gradual decrease of the average grain size and a drastic increase of electrical resistivity was observed in all samples investigated when the oxygen pressure was increased during sintering. For example, on changing the oxygen pressure during sintering of 0.2 at % doped samples from 0.02 (air) to 0.5 MPa, the electrical resistivity increased by about more than four orders of magnitude, while the average grain size decreased by about 70%. Thus, an oxygen atmosphere during grain growth is important and determines the defect concentration. At high concentrations of cation vacancies, induced at high oxygen pressure, the ionized donors are mainly compensated by ionized cation vacancies, which decrease the effective number of charge carriers, leading to high electrical resistivity [1].

Particular interest was devoted to 0.4 at % doped samples which showed anomalous grain growth. In Fig. 6 the average size of anomalously grown grains as a function of sintering time are shown at two oxygen

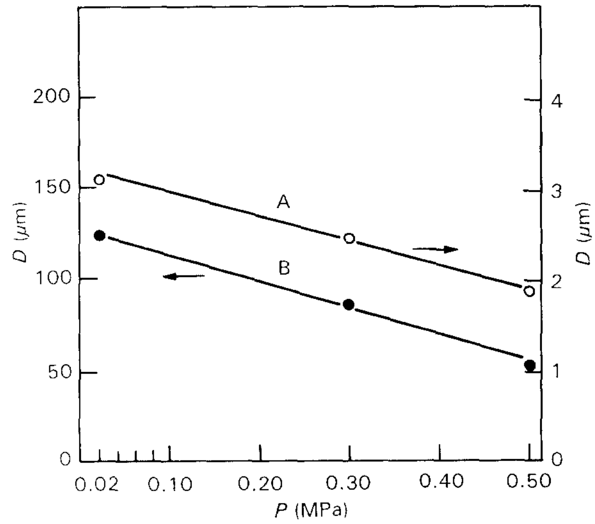

Figure 4 Average grain size versus partial pressure of oxygen of (○) 0.2 at % doped sample, curve A; and (●) of anomalous grains in 0.4 at % doped sample, curve B, sintered at 1280 °C for 20 h.

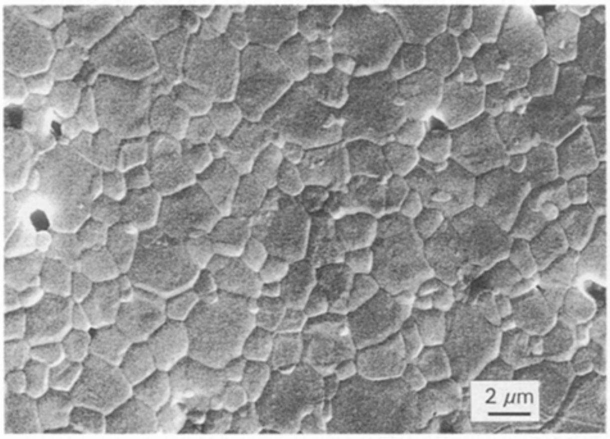

Figure 5 Microstructure of 0.2 at % doped sample sintered at 1280 °C for 20 h at 0.5 MPa oxygen pressure.

partial pressures. The average grain size was followed from the time when nucleation started, to the time when the grains started to impinge on each other and hinder anomalous grain growth.

A linear dependence of grain size versus time was found in the investigated range. This is in accordance with the general rule that the growth rate of large grains in fine grained matrix is constant [17]. Samples sintered at higher oxygen pressure exhibited a slower grain growth rate, again demonstrating the inhibiting influence of increasing oxygen pressure on the transport properties of donor doped $BaTiO_3$.

Sintering and grain growth in solid state are governed by the diffusion rate of the slowest moving species, which in turn depends on the concentration of vacant lattice sites. With increasing oxygen partial pressure, the concentration of oxygen vacancies in doped $BaTiO_3$ decreases, resulting in slower transport of oxygen ions. The defect chemistry model, based upon electrical conductivity measurements, predicts a decrease in amount of oxygen vacancies with increasing donor concentration and/or oxygen partial pressure. Fig. 7 shows the concentration of oxygen vacancies in donor doped $BaTiO_3$ at 1340 °C as a function of oxygen partial pressure and donor concentration, calculated using mass action constants from [6]. This predicted decrease in the concentration of oxygen vacancies coincides with the inhibition of grain growth in donor doped $BaTiO_3$. The observed experimental evidence supports the conclusion that the transport properties in *n* doped $BaTiO_3$ depend on the presence of oxygen vacancies, as already proposed by Anderson [18].

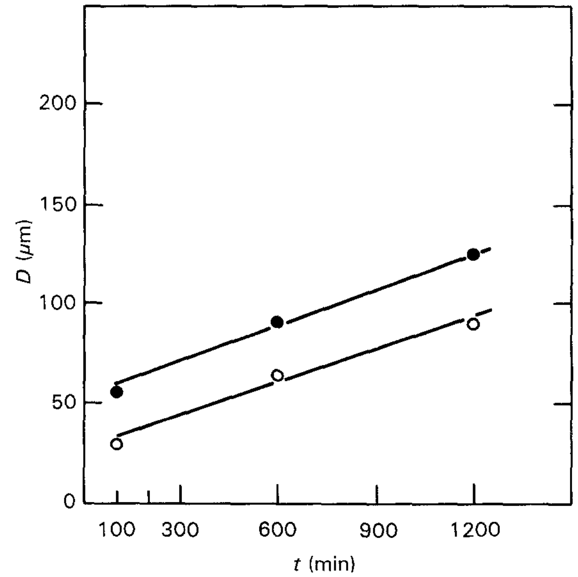

Figure 6 The average size of anomalous grains in 0.4 at % doped samples sintered in air and at (●) 0.02 and (○) 0.3 MPa oxygen pressure versus the time of sintering.

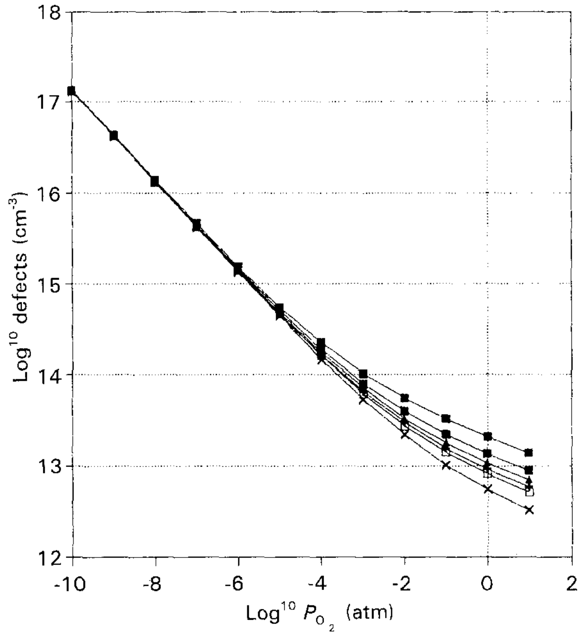

Figure 7 Dependence of oxygen vacancy concentration $[V_O]_{tot}$ in donor doped $BaTiO_3$ on oxygen partial pressure and donor dopant amount at 1340 °C: (■) 0.2, (■) 0.4, (▲) 0.6, (+) 0.8, (□) 1.0 and (×) 2.0 at % La, respectively.

4. Conclusions

The microstructure development of donor doped $BaTiO_3$ during sintering in the solid state can be controlled by the oxygen partial pressure.

The donor dopant concentration which blocks the anomalous grain growth in subsolidus grain growth can be determined by the relation $C_D = K_{111} \times 6\, V/D$ [5].

The grains which undergo the anomalous grain growth process are semiconducting.

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