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Temperature dependence of the coarsening behavior of (Ba, Sr)TiO_3 grains dispersed in a SiO_2-rich liquid matrix

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Abstract

The shape of $(Ba_{0.35}Sr_{0.65})TiO_3$ (BST) grains and their coarsening behavior were investigated as a function of temperature. The BST grains exhibit a morphological change at approximately 1410 °C; the grains were angular at 1390 °C and corner-rounded at 1420 °C. At 1390 °C, a few very large grains appear in the microstructure. Such abnormal grain growth is explained in terms of a coarsening advantage due to the $\Sigma3$ coincident site lattice (CSL) boundaries. On the other hand, at 1420 °C, normal grain growth was observed to occur. The change in coarsening behavior with temperature is related to the structural transition of the interface.

Keywords: Abnormal grain growth; (Ba, Sr)TiO_3; Grain growth; Microstructure-final; Coincidence boundaries

1. Introduction

For ceramic solid grains dispersed in a liquid matrix, the overall interfacial energy of the system is minimized by grain coarsening, which usually occurs in two different ways: normal grain growth (NGG) and abnormal grain growth (AGG). During NGG, the average grain size increases continuously without changing the normalized size distribution. However, in AGG, a few large grains develop and grow rapidly at the expense of small matrix grains. In both cases, the grain coarsening occurs at the solid/liquid interface. As a result, the interfacial structure determines the coarsening mechanism as well as the coarsening rate. Note also that the two extreme models of the interface structures are atomically smooth and atomically rough.[1]

For spherical solid grains with an atomically rough interface structure, the coarsening process is controlled by diffusion through the liquid phase because atomic attachment at the interface has little energy barrier. For the angular grains, on the other hand, the interfaces are atomically smooth. As a result, the attachment of an atom to the interface produces excess broken bonds. Therefore, a significant energy barrier for atomic attachment is expected, such that ledge-generating sources like 2-dimensional (2-D) nuclei are necessary for growth. This process has been suggested as the mechanism of AGG because only a few large grains with sufficient driving force to induce 2-D nucleation can grow.[2–11] Note that AGG is indeed observed to occur only for angular grains with atomically smooth interfaces.

In fact, Herring[12] suggested earlier in his classic paper that the growth of an atomically smooth plane would require a 2-D nucleation process. Furthermore, he tacitly explained AGG by suggesting a discontinuous variation in grain coarsening behavior if coarsening occurs by 2-D nucleation. Wynblatt et al.[13,14] also explained the coarsening of Pt particles on alumina substrate by the "nucleation inhibited" growth process. Although they did not mention AGG during liquid-phase sintering, their works are believed to form the basis of the 2-D nucleation controlled coarsening process.

On the other hand, the shape of solid grains or the interface structure has been reported to vary by a small change either in temperature[3,6] or in composition.[9] In particular, the change in interface structure from atomically smooth to rough is known[15] to occur discontinuously at the roughening transition temperature

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(T_R), as predicted by Burton et al.[16,17] Such a transition of the interface structure with temperature has been observed in $BaTiO_3$,[3,5,6] and in other systems.[18–21] In this paper, the roughening transition of the interface structure observed in $(Ba_{0.35}Sr_{0.65})TiO_3$ (BST) ceramics is reported. Consequent changes in the grain coarsening behavior were examined and related to the relevant coarsening mechanism.

2. Experimental procedure

The starting $(Ba_{0.35}Sr_{0.65})TiO_3$ powders were prepared by mixing of $BaTiO_3$(Sakai Chemical Industry Co., Ltd., Osaka, Japan) and $SrTiO_3$(TAM Ceramics, Niagara Falls NY, USA) with 2 mol% of SiO_2(Aldrich Chemical Co., Milwaukee, WI, USA). The addition of SiO_2 during sintering of $BaTiO_3$ is known[2] to result in the formation of a liquid at relatively low temperature by lowering the eutectic temperature. The mixed powders were ball-milled in ethanol with zirconia balls for 24 h, and calcined at 900 °C for 2 h. The obtained powders were lightly compacted into 8 mm-diameter cylindrical specimens and then pressed hydrostatically at 100 MPa.

The compacts were heated at a rate of 130 °C/min and sintered at 1390 °C and 1420 °C, respectively. The sintering time was varied from 5 to 15 h. The cross-section of the sintered specimens were polished and etched with dilute HCl containing a small amount of HF. Scanning electron microscopy (SEM) was used for the microstructure observation. The grain orientation was determined using electron back scattered diffraction (EBSD) (Oxford/Link Opal, England). The average grain size was determined by multiplying 1.775 to the mean intercept length.[22]

3. Results and discussion

Fig. 1(a) and (b) show the microstructures of a typical BST specimen sintered at 1390 °C for 5 and 15 h, respectively. As can be observed, a few grains have grown exceptionally, and the microstructures show the region where the largest abnormal grain exists in each specimen. The grain shape is angular with sharp corners, which suggests that the interface structure is atomically smooth. After sintering for 5 h [Fig. 1(a)], the average size of the matrix grains was determined to be 11 μm and the largest abnormal grain was ~200 μm. During further heat-treatment for 15 h [Fig. 1(b)], the size of the matrix grains remained constant but the abnormal grains have grown continuously; abnormal grains up to ~2000 μm appeared. Therefore, the coarsening rate of the abnormal grains at this temperature was ~180 μm/h, which is almost the same as reported for $BaTiO_3$.[23] Pores trapped inside the abnormal grain are the consequence of such a rapid interface migration.

For the abnormally grown BST grains in Fig. 1, re-entrant angles were observed at the interfaces without exception, as indicated by arrows. When single crystals are in thermodynamic equilibrium, they always exhibit convex planes. Therefore, the presence of re-entrant angles may indicate that the abnormal BST grains observed consist of several grains. Indeed, the presence of grain boundaries formed by a trapped grain can be noted through a careful observation on Fig. 1(a) (inside the circle).

Fig. 2(a) is the orientation map at the region of the abnormal grain in Fig. 1(a). The figure shows that the abnormal grain consists of three different grains separated either by a Σ3 or a Σ9 CSL boundary; the boundary between the grains at the left- and right-hands was mostly Σ3 CSL and that of the trapped grains was either a Σ3 or a Σ9 CSL boundary. Concerning the geometric interaction,[24,25] Σ9 boundaries can be regarded as $\Sigma 3^n$ twin-related variants as illustrated schematically in Fig. 2(b). According to Forwood et al.[26,27] and others,[28,29] the Σ9 boundary may dissociate into two symmetric (111) tilt Σ3 grain boundaries or change to (112) tilt Σ3 grain boundary.

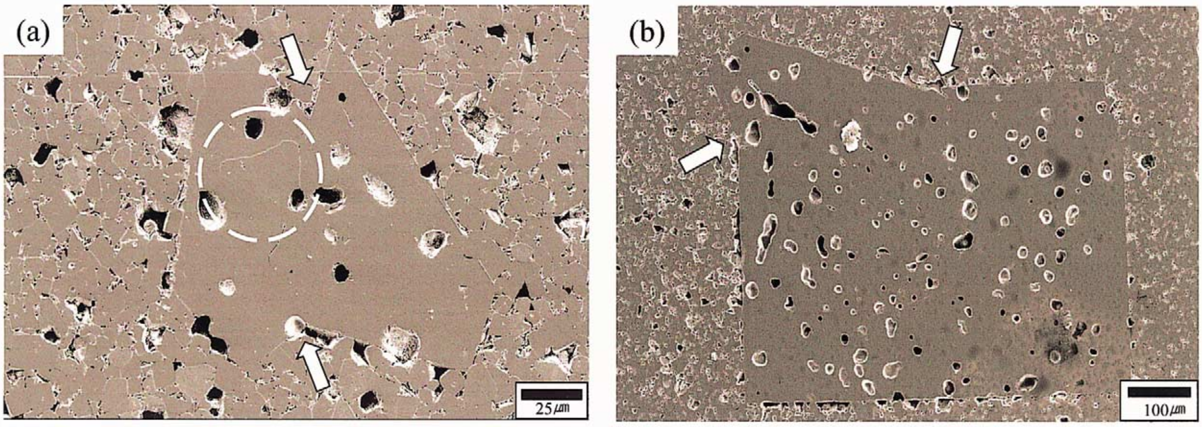

Fig. 1. SEM micrographs of the specimen sintered at 1390 °C for (a) 5 h and (b) 15 h.

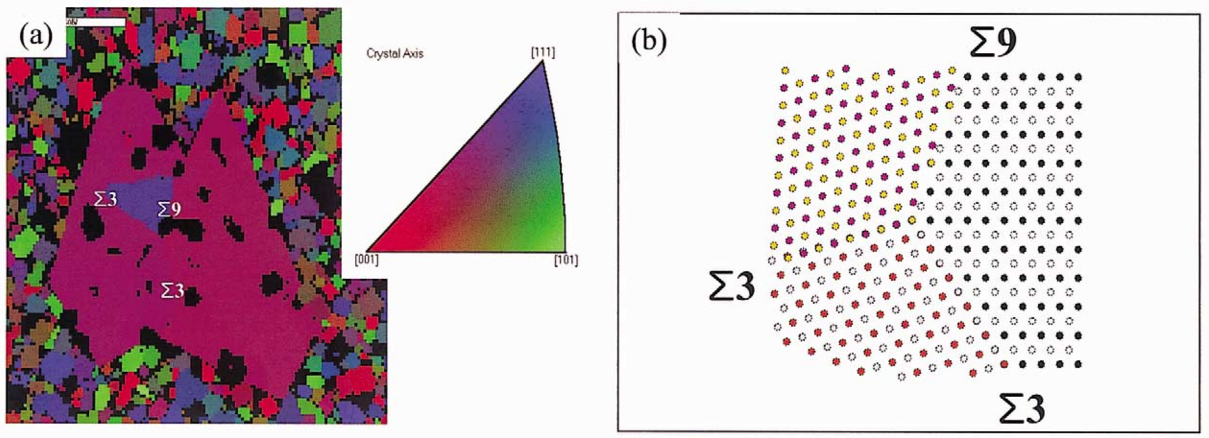

Fig. 2. (a) EBSD orientation map for the abnormal grain in Fig. 1(a), and (b) the schematic illustration of the Σ3 and Σ9 CSL boundaries.

When abnormal grain growth occurs, the re-entrant edges created by the twins were suggested[3–6,8,30] to play a critical role. The coarsening of angular grains like BST in this experiment occurs by a 2-D nucleation and lateral growth mechanism, and defects such as twins provide perpetual and favorable sites for 2-D nucleation. Therefore, as already observed in PMN-PT ceramics,[8] grains with a re-entrant Σ3 CSL boundary grow exceptionally because they can grow with a very small driving force.

On the other hand, it is known that an atomically smooth interface structure changes to an atomically rough one at higher temperatures. When this occurs, the grain shape changes from being angular to spherical, and grain coarsening by 2-D nucleation no longer operates. Note that the anisotropy in the interface energy becomes negligible because the interface structures regardless of crystallographic direction are atomically rough. Under this condition, there is practically no energy barrier for the attachment of atoms. Mass transfer by diffusion through the liquid phase governs the overall coarsening process and the coarsening rate is linearly proportional to the driving force. This means that, regardless of the magnitude of the driving force for grain growth, all grains larger than a certain critical size can grow so that the normal grain growth results.

Fig. 3(a) and (b) show the microstructures of the BST specimen sintered at 1420 °C for 5 and 15 h, respectively. Although the difference in the sintering temperature between the specimens shown in Figs. 1 and 3 is relatively small, the grain coarsening behaviors at these two temperatures are quite different. Note that the grains usually exhibit rounded corners and no abnormal grain growth occurred at 1420 °C. At this temperature, the average grain size after sintering for 5 h was determined to be 29 μm [Fig. 3(a)]. It increased to 36 μm after sintering for 15 h [Fig. 3(b)]. In NbC–Co,[31] it has been also reported that the grains with rounded corners do not show AGG behavior.

The results may indicate that, for a BST crystal, the roughening transition of the interface structure occurs at a very narrow temperature range of 1390–1420 °C. The transition of interface structure and its effect on grain coarsening was further verified. For this purpose, the specimen was sintered at 1390 °C for 5 h. It was then continuously heated at 1420 °C for another 10 h. Fig. 4(a) shows the largest grain observed from the specimen. For this specimen, the average size of the matrix

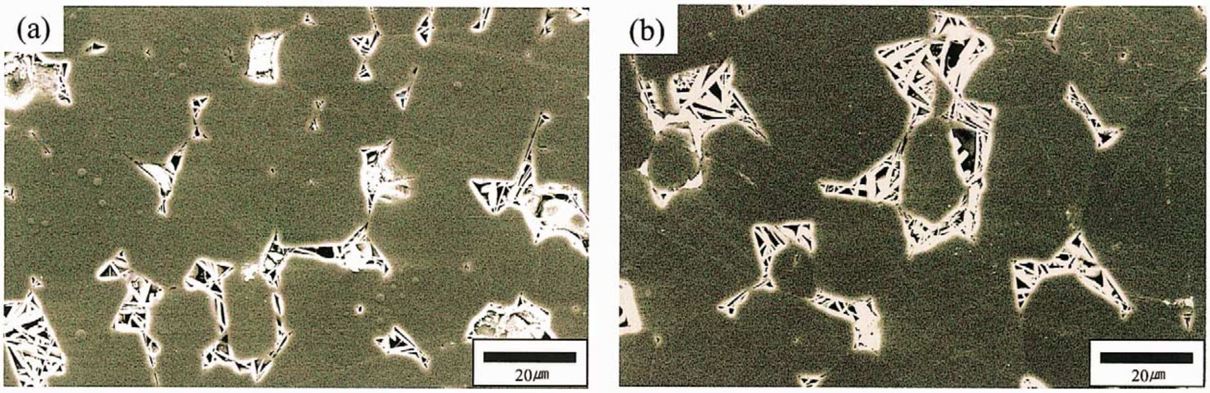

Fig. 3. SEM micrograph of the specimen sintered at 1420 °C for (a) 5 h and (b) 15 h.

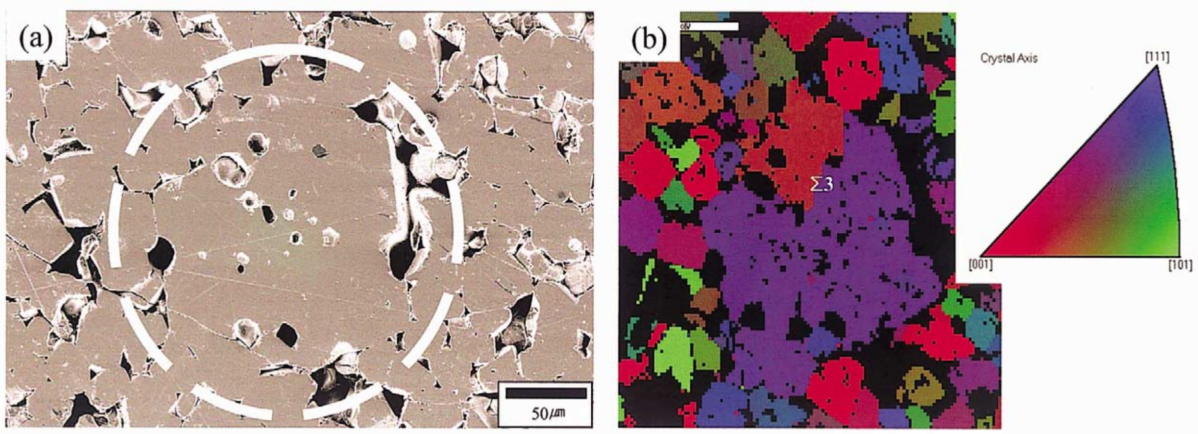

Fig. 4. (a) SEM micrograph of the specimen sintered initially at 1390 °C for 5 h and another 10 h at 1420 °C, and (b) the EBSD orientation map.

grains was 36 μm, which is practically the same with that of the specimen shown in Fig. 3(b). On the other hand, the largest grain was approximately 270 μm, which is slightly larger than the abnormal grain in Fig. 1(a). The growth rate of the largest grain at this temperature was therefore ~7 μm/h, which is much smaller than ~180 μm/h at 1390 °C.

This suggests that extensive coarsening is only possible at 1390 °C. Fig. 4(b) is the orientation map of the same region shown in Fig. 4(a). It has been again confirmed that the large grain has a Σ3 CSL boundary. However, the re-entrant edges formed by the Σ3 CSL boundary did not provide a coarsening advantage because of the change in the coarsening mechanism. At 1420 °C, the coarsening process is not controlled by 2-D nucleation but by diffusion through the liquid. For a diffusion controlled coarsening process, it has been reported[10,32] that the growth rate of a very large grain is rather slow compared to that of the matrix growing grains. As a result, a very large grain introduced initially merges gradually into a uniform grain size distribution.

4. Conclusion

BST grains at 1390 °C were angular, and showed an abnormal grain growth behavior. The re-entrant edges formed at the Σ3 CSL boundaries were suggested to cause such an abnormal behavior. However, at 1420 °C, the shape of the BST grains became corner-rounded, and no abnormal grain growth occurred. Furthermore, the initially large grain with the Σ3 CSL boundary did not grow excessively at this temperature. Such a change in the coarsening behavior which is likely to be due to a roughening transition of the BST interface structure, occurred in a narrow temperature range between 1390 and 1420 °C. The results show that, at the temperature range where the roughening transition occurs, temperature control is rather critical for microstructure development.

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