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Abnormal grain growth of $BaTiO_3$ by 2D nucleation and lateral growth

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Abstract

The microstructure of abnormal grains in $BaTiO_3$ based ceramics suggests that 2D nucleation and lateral growth take place in the material. High-resolution transmission electron microscopy investigation reveals that nucleation takes place at triple junctions of abnormal grain and adjacent matrix grains, subsequently form steps and the steps grow laterally along {1 1 1} planes of the abnormal grains. The abnormal grain boundaries are faceted in the growth direction, however, the ledges, which possess boundaries deviated from low-index crystallographic planes of the abnormal grains, could provide high mobility necessary for abnormal grain growth.

Keywords: Electron microscopy; Grain growth; $BaTiO_3$; Abnormal grain growth

1. Introduction

Abnormal grain growth (AGG) often takes place in $BaTiO_3$ based ceramics during the sintering process.[1–6] It has been reported that AGG occurred in TiO_2-excess materials, while normal grain growth was observed in BaO-excess ones.[1,4] Since {1 1 1} twin lamellae were observed in abnormal $BaTiO_3$ grains almost exclusively, the twin plane reentrant edge (TPRE) is generally accepted as the mechanism for AGG in $BaTiO_3$.[7,8] Meanwhile, faceting was observed at most of grain boundaries (GBs) in AGG $BaTiO_3$.[9–11] Kang and co-workers[5,9,12,13] observed that, when the sintering atmosphere was changed from oxidizing to reducing ambient, the grain growth changed from AGG to normal grain growth, while GBs of $BaTiO_3$ transited from faceted to rough. Therefore, a strong correlation between the faceting and AGG was proposed, while it was suggested that {1 1 1} twin lamellae appeared only to enhance the growth of abnormal grains along the twin lamellae when GBs were faceted.[9] A series of AGG materials, which presented faceted GBs, have been studied and it was proposed that AGG was applied by two-dimensional (2D) nucleation and lateral growth in these materials,[14–17] although 2D nucleation and lateral growth was rarely discussed on AGG of $BaTiO_3$ based ceramics in the literature.[18,19] As these materials usually have atomically smooth interfaces or GBs, where nucleation is extremely difficult, ledges or screw dislocations are usually necessary for the AGG.

In this work, triple-grain junctions and small steps of the abnormal GBs are investigated by transmission electron microscopy (TEM) in Y-doped $BaTiO_3$ ceramic, and the 2D nucleation and lateral growth mechanism is discussed as the mechanism of AGG of the $BaTiO_3$ material.

2. Experimental procedure

Polycrystalline Y-doped $BaTiO_3$ sample was prepared by the conventional mixed-oxide method. High purity $BaCO_3$, TiO_2 and Y_2O_3 powders (Sinopharm Chemical Reagent Ltd., Shanghai, China) were mixed with a nominal mole ratio of 1.000:1.001:0.002. The mixture was calcined at 1050 °C for 10 h and milled in agate mortar, while this procedure was repeated for three times. After that, the powders were dry-pressed into pellets (diameter 20 mm and thickness 1 mm) with a pressure of 20 MPa. The pellets were then sintered in air at 1250 °C and 1300 °C for 24 and 10 h. The nominal heating and cooling rates were 5 °C/min in the whole experiment.

Sintered sample was polished and etched in a solution of 95H_2O-4HCl-1HF (vol.%) for optical microscopy observation. Thin foil specimens for TEM were prepared by the conven-

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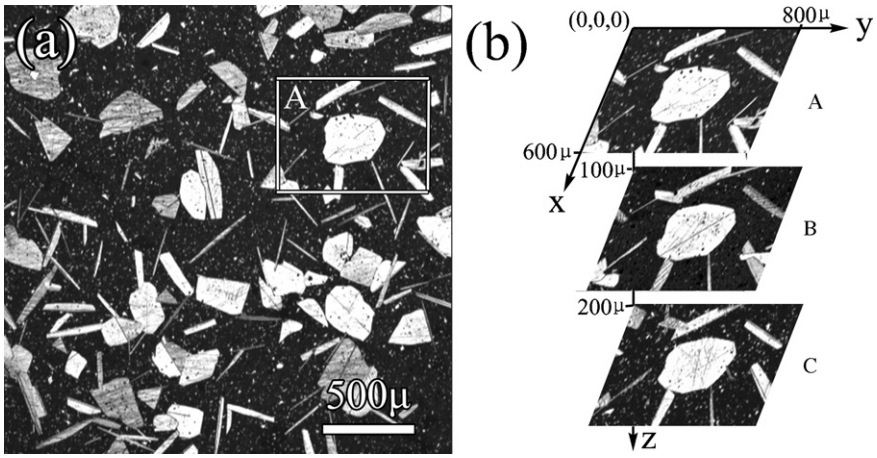

Fig. 1. (a) Optical micrograph of Y-doped $BaTiO_3$. (b) Series of optical micrographs of the area marked with A in (a), where the micrographs were taken at series of interior sections with depths of 0, 100 and 200 μm. The large abnormal grain in the center of the micrographs maintains equiaxed geometry in all interior sections.

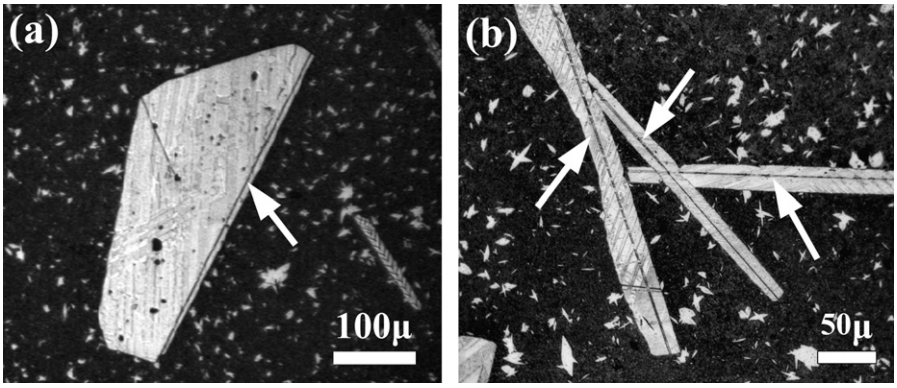

Fig. 2. Optical micrographs of two typical geometries of the abnormal grains: (a) equiaxed; (b) elongated. The {1 1 1} twin lamellae are indicated by arrows.

tional ion-milling method. A Tecnai G^2 F30 TEM (FEI Co., Eindhoven, Netherlands), which was operated at 300 kV and equipped with an X-ray energy-dispersive spectrometer (EDS), was used for investigation of microstructure and chemical composition.

3. Results

Abnormal grains were observed in the Y-doped $BaTiO_3$ as shown in Fig. 1. The size of the abnormal grains is about one thousand times of that of the matrix grains, which is ~300 nm in diameter. The abnormal grains possess two kinds of geometry, one is elongated and the other is equiaxed, although both of them have {1 1 1} twin lamellae and flat GBs. The geometry of the abnormal grains was confirmed by observation at a series of interior sections at evenly-spaced depths of the specimen (Fig. 1b). Typical abnormal grains are shown in Fig. 2, where the {1 1 1} twin lamellae are indicated by arrows. It is noticeable that the abnormal grains are not even at the two sides of the twin lamellae. TEM micrograph (Fig. 3) shows a faceting abnormal GB, where the abnormal grain was tilted in ⟨1 1 0⟩ zone axis, while terraces and ledges were observed parallel to the {1 1 1} and {1 1 0} planes of the abnormal grain, respectively.

HRTEM images of the GB structures between abnormal and matrix grains were shown in Fig. 4, where abnormal grain was presented at lower part of each micrograph. Fig. 4a shows a triple junction between the abnormal grain and two matrix grains. A plateau (marked with P in Fig. 4a) was observed formed on the

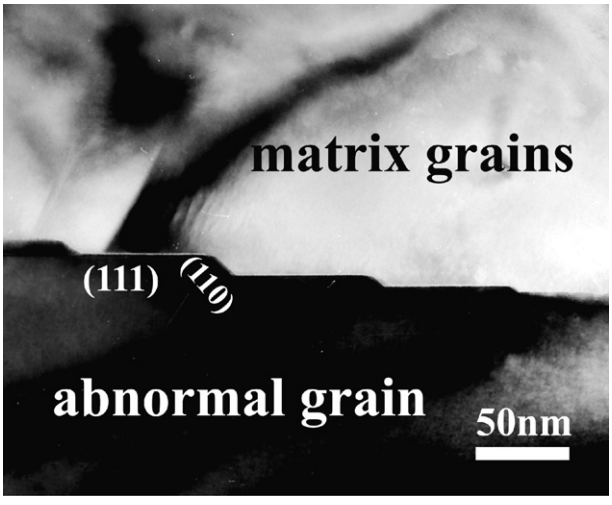

Fig. 3. TEM image showing a grain boundary (GB) between an abnormal grain and matrix grains.

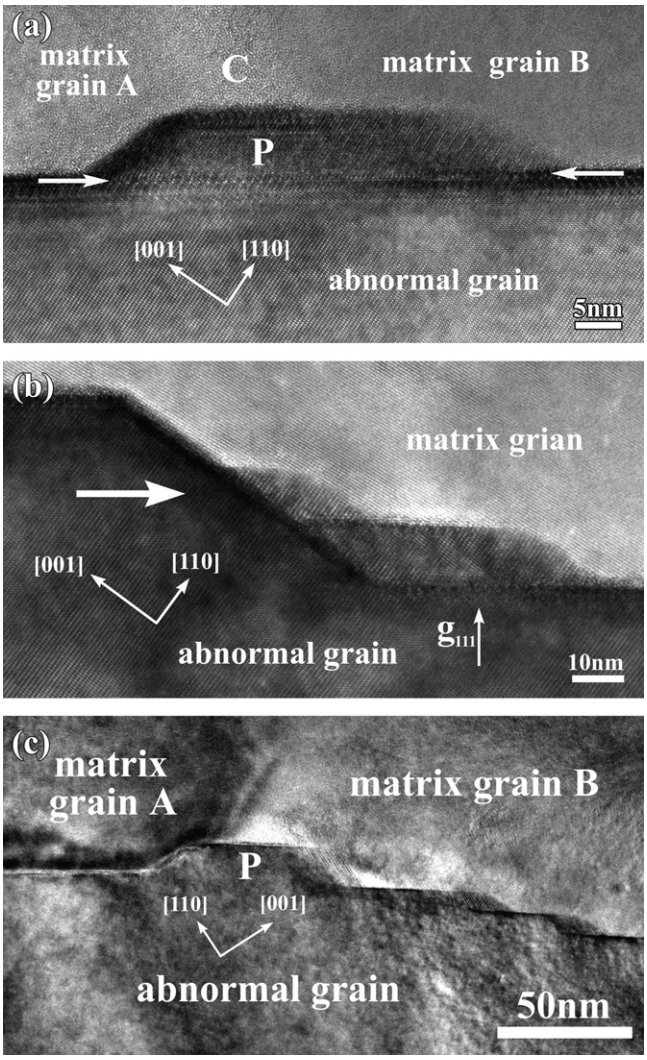

Fig. 4. HRTEM images of plateaus and ledges at triple-grain junctions and faceted GBs. (a) A protruding plateau formed on the (1 1 1) plane of an abnormal grain at a triple junction of the abnormal grain C and two matrix grains A and B. The boundary between grains A and B is also faceted. (b) Ledges formed at reentrant angle of faceted GBs. (c) A plateau at triple junction of $BaTiO_3$ grains.

(1 1 1) plane of the abnormal grain, whereas it has flat boundaries with the adjacent matrix grains. Similar to the plateau, ledges were also observed at reentrant angle of faceted GBs (e.g. Fig. 4b), while their height was determined as ~10 nm. Straight boundary lines could be seen between the ledges (or the plateau) and the abnormal grains (e.g. the boundary line indicated by a pair of arrows in Fig. 4a, and the boundary lines clearly visible between the ledges and the abnormal grain in Fig. 4b). However, these boundary lines in HRTEM images were rather artifacts caused by the projection of the GBs (e.g. terrace planes) between the abnormal grains and the neighbor matrix grains in the viewing direction. Because the interfaces (i.e. ledge planes) between the ledges (or the plateau) and the matrix grains were deviated far from the (1 1 0) plane of the abnormal grain, which is edge-on in the incident direction of the electron beam, parts of the GBs between the abnormal grains and the matrix grains were projected into the lattice-fringe images of the ledges (or the plateau). As demonstrated in Fig. 4c, which shows another plateau in triple-grain junction, when the ledge plane of the left side of the plateau was only slightly deviated from the (1 1 0) plane of the abnormal grain, which is edge-on in the incident beam direction, the boundary line disappeared in HRTEM micrograph. Because of the different orientations of the matrix grains, the ledge planes lie on different crystallographic planes of the abnormal grain, while most of them deviate from low-index crystallographic planes of the abnormal grains. For example, in Fig. 4a that, comparing to the overlapped region between the plateau and matrix grain A, the overlapped region between the plateau and matrix grain B is larger and shows obvious Moiré fringes, where the contrast of the lattice fringes in the overlapped region fades from the center to the edge of the plateau. It suggests that the ledge plane between the plateau and matrix grain A is not the same orientation as that between the plateau and matrix grain B. Similar features could also be seen in other HRTEM micrographs. Small amount of intergranular phase was located at triple-grain junctions as marked with C in Fig. 4a as well as GBs. The composition of the intergranular phase was determined by EDS that the concentrations of Y and Si were below 1 at.% and 3 at.%, respectively.

4. Discussion

Most of the abnormal GBs were observed faceting with the long segments of the facets along the {1 1 1} planes and the short ones along the {1 1 0} planes of the abnormal grains, which agrees with previous reports in the literature.[3,10] This is attributed to that the {1 1 1} and {1 1 0} planes are close-packed planes of $BaTiO_3$. However, nucleation is difficult to take place on these planes, as it raises high surface energy. Therefore, reentrant angles are usually necessary for the nucleation of $BaTiO_3$ grain growth.[8,20] In TPRE mechanism, the reentrant angle located on the twinning planes between two adjacent {1 1 1} planes provides the sites for nucleation, which makes the TPRE an important mechanism for AGG of $BaTiO_3$ ceramics.

Besides the TPRE mechanism, 2D nucleation and lateral growth is also considered for the AGG of $BaTiO_3$ in this work. Lee et al.[9] have shown that, comparing to abnormal grains containing {1 1 1} twin lamellae, which correspond to the TPRE growth, 2D nucleation and lateral growth on {1 1 1} planes exhibited same probability at usual sintering temperatures between 1250 and 1350 °C. The mechanism of 2D nucleation and lateral growth on close-packed plane has been discussed theoretically and experimentally in a variety of materials[5,14–16,18,19,21]; nevertheless, we recapitulate here the essential issues that are needed for understanding the AGG of $BaTiO_3$ ceramics in this work. The 2D nucleation barrier should be overcome by the driving force for abnormal grain growth, which may be attributed to different curvatures of the GBs.[22] Theoretically, nucleation rate on the {1 1 1} planes is proportional to the surface area of the {1 1 1} planes, i.e. with larger surface more nuclei could form on the {1 1 1} planes.[20] However, in contrast to solid–liquid system where opportunity of 2D nucleation is evenly at all solid–liquid interface[14,15,23]; in this work, where there is only a small amount of intergranular phase (or liquid phase) at GBs during sintering, 2D nucleation prefer to

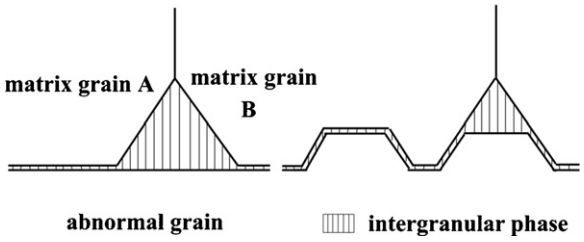

Fig. 5. Schematic illustrations of nucleation at a triple-grain junction and a GB in $BaTiO_3$ based ceramics. The left figure is before nucleation and the right one is after that. Small amount of intergranular phase is located at the triple-grain junction and the GB. Assuming that the nuclei have the same size at the triple junction and the GB, while the atoms for nucleation come from the neighbor matrix grains, the change of the free energy associated with the nucleation can be simplified as $\Delta G = -V\Delta G_v + \Delta G_{IF} = -V\Delta G_v + \Delta A\gamma$. Here, ΔG is the change of the total free energy, ΔG_v is the change of the volume free energy of the nucleation atoms caused by the capillary pressure difference between the abnormal grain and matrix grains, V is the volume of the nucleus, ΔG_{IF} is the change of the total interfacial energy, ΔA is the change of the surface area, and γ is the interfacial energy per unit area. When nucleus forms at the GB, the change of the free energy is $\Delta G_{GB} = -V\Delta G_v + \Delta G_{IF} = -V\Delta G_v + \Delta G_A^{IF} + \Delta G_M^{IF}$; on the other hand, when nucleus forms at the triple-grain junction, the change of the free energy is $\Delta G_{TGJ} = -V\Delta G_v + \Delta G_{IF} = -V\Delta G_v + \Delta G_A^{IF}$, where ΔG_A^{IF} corresponds to the change of the interfacial energy between the abnormal grain and the intergranular phase, and ΔG_M^{IF} corresponds to that between the matrix grain and the intergranular phase.

take place at triple-grain junctions. This is suggested by Fig. 4a and c, where the plateaus are corresponding to the nuclei formed at the triple junctions between the abnormal grains and adjacent matrix grains. The reason that the nucleation prefers the triple-grain junctions to flat GBs (or terraces) could be explained by the different changes of the free energy associated with the nucleation at these sites. Fig. 5 is schematic illustrations of nucleation at a triple-grain junction and a flat GB. By assuming the shape and volume of the nuclei are the same and the atoms needed for nucleation are coming from the neighbor matrix grains, the difference of the changes of the free energy associated with the nucleation at these two sites could be simplified as the changes of the total interfacial energy generated by the nucleation. Therefore, the change of the free energy associated with the nucleation at the triple-grain junction is much less than that of the flat GB (or the terrace), hence, nucleation is preferred to take place at triple-grain junctions. The nuclei will form plateaus and subsequently grow up laterally on the close-packed plane, as a result, form faceted GBs with adjacent matrix grains. This agrees with the suggestion that the faceted GB is directly related to the neighbor triple-grain junctions.[8,12] If liquid films with adequate thickness are present at all GBs of $BaTiO_3$, which is different from this work, 2D nucleation may take place at GBs similar to that at triple-grain junctions.

The migration rate of the ledge strongly depends on the GB orientation and the growth direction.[22,24] In Fig. 4b, the horizontal arrow denotes the growth direction of the faceted GB located in the left part of Fig. 4b. The faceted GB is edge-on in the $[1\,\bar{1}\,0]$ zone axis and parallel to the (1 1 0) plane of the abnormal grain, while the (1 1 0) plane is a singular plane[10] and not favored for lateral growth. Two ledges, which have boundaries deviating from low-index crystallographic planes, formed at the reentrant angle between two facted GBs. It suggests that these ledges have higher mobility than that of the faceted GB.[22,24] Meanwhile, most of the ledges are ~10 nm high, indicating that the height of ledges could also influence the GB migration. The existence of kinks in the ledges is possible, however, it could not be directly observed by current HRTEM investigation.

5. Conclusions

AGG has been studied by TEM techniques in $BaTiO_3$ based ceramics. The results revealed that 2D nucleation and lateral growth took place in the AGG of $BaTiO_3$ as well as the TPRE mechanism. Nuclei were formed at triple-grain junctions and lied on $\{1\,1\,1\}$ planes of the abnormal grains, after that the nuclei grew into steps and consequently grew laterally. The ledge planes are deviated from low-index crystallographic planes of the abnormal grains and the height of the ledges is about 10 nm.

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