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Fabrication of $BaTiO_3$ single crystals using secondary abnormal grain growth

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Abstract

During secondary abnormal grain growth (SAGG) of $BaTiO_3$, some grains were observed to grow extensively. This phenomenon has been implemented for the fabrication of $BaTiO_3$ single crystals. When a $BaTiO_3$ powder compact was sintered at 1365°C, a small number of secondary abnormal grains appeared. The sintered specimen was then further heat-treated at 1355°C. At this temperature, the preexisting secondary abnormal grains continued to grow without forming the new ones. $BaTiO_3$ single crystals larger than 1 × 1 cm could thus be obtained by such a two-step heat-treatment.

Keywords: Abnormal grain growth; $BaTiO_3$; Grain growth; Microstructure-final; Sintering; Titanates

Abnormal grain growth (AGG) has been used for the fabrication of single crystals of various metallic materials,[1–5] manganese zinc ferrite,[6] barium titanate,[7,8] and PMN-PT.[9] This process is usually referred to as the solid-state single crystal growth because melting of the major components is not involved. As a result, this method is highly promising particularly for materials with a high melting temperature, phase transition, volatile elements, and incongruent melting.

Recently, Lee et al.[10] have reported that the secondary abnormal grain growth (SAGG) occurs in $BaTiO_3$. At a narrow temperature range between 1360°C and 1370°C, very large $BaTiO_3$ grains appeared from the coarse and uniform-grained matrix which previously resulted from the primary abnormal grain growth. The growth of secondary abnormal grains is limited when they impinge each other. As a consequence, the final size of secondary abnormal grains is inversely proportional to their number density. This suggests the possibility of single crystal growth. The major concern is to limit the number density of secondary abnormal grains. The aim of this communication is to report a simple way for controlling the nucleation of secondary abnormal grains and to fabricate $BaTiO_3$ single crystals.

All details of the experimental procedure are identical to those reported earlier.[10] The rectangular powder compacts (20×20 mm) of 2 mm in height were prepared by uniaxial pressing at 1 MPa followed by hydrostatic pressing at 200 MPa. As SAGG of $BaTiO_3$ was observed[10] to occur only at temperatures ranging from 1360°C to 1370°C, the powder compacts were sintered at 1365°C for various periods in air. After sintering, the specimens were again heat-treated at 1355°C for up to 100 h. The heating and cooling rate was 4 °C/min.

Fig. 1 shows the overall microstructure of the polished and chemically etched surface of a $BaTiO_3$ specimen sintered at 1365°C for 15 h. Appearance of some giant grains of several millimeters in size is clearly discerned. The number density of giant grains, N_A, that resulted from SAGG was about 8.5/cm^2. It has been previously reported[10] that SAGG did not occur when the temperature is slightly lowered. After sintering at 1355°C for 15 h, no secondary abnormal grain ($N_A = 0$) was observed. Furthermore, sintering at 1365°C for 5 h also exhibited $N_A = 0$, which indicates that there is an induction period for SAGG. In this respect, N_A is expected to be a function of heat-treatment time.

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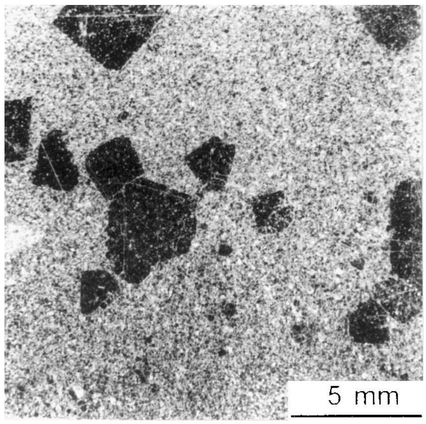

Fig. 1. Microstructure of a $BaTiO_3$ specimen sintered at 1365°C for 15 h in air.

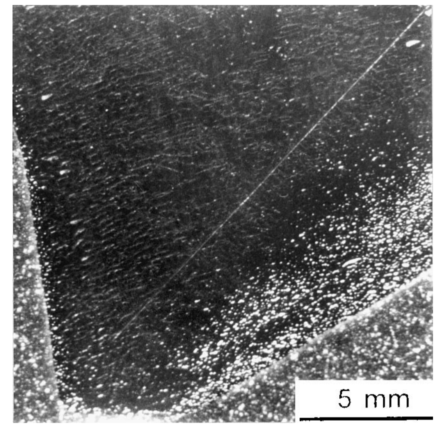

Fig. 3. Microstructure of a $BaTiO_3$ specimen sintered at 1365°C for 1 h and then heat-treated at 1355°C for 100 h.

Although the heat-treatment at 1365°C for less than 5 h did not result in notable SAGG, the nuclei of secondary abnormal grains are expected to be formed during this stage and can be discerned if their growth is promoted. Fig. 2(a) and (b) shows the surface microstructure of a specimen heat-treated at 1365°C for 1 h and 3 h, respectively. They were then further heat-treated at 1355°C for 20 h. Note at this temperature that the nuclei for SAGG did not form, but only preexisting ones have grown. As observed, the specimen sintered at 1365°C for 3 h [Fig. 2(b)] has more secondary abnormal grains than that sintered at 1365°C for 1 h [Fig. 2(a)]. In the latter case, only one grain has grown up to 6 mm in size. New secondary abnormal grains did not appear during the treatment at 1355°C.

Fig. 3 shows the surface microstructure of a specimen heat-treated at 1355°C for 100 h after sintering at 1365°C for 1 h. From the upper right corner of the specimen, one secondary abnormal grain was nucleated during the first heat-treatment and then continued to grow during the second heat-treatment. The size of this secondary abnormal grain or single crystal was approximately 2 cm. In this method, the duration of the second heat-treatment mainly determines the size of the single crystal. Fig. 4 shows the optical quality of obtained 1-mm thick $BaTiO_3$ single crystal.

At the center of the grown single crystal in Fig. 3, two parallel lines were observed. Such two parallel lines were always observed in secondary abnormal grains and are known to be a (111) double twin, as reported by Lee et al.[10] In the polycrystalline part of the specimen (Fig. 3) matrix grains were angular and a small amount of liquid phase was observed between angular grains.[10] The angular shape of grains indicated that the solid-liquid interface structure was atomically smooth and thus the coarsening of grains proceeded by the lateral growth. When the grain coarsening proceeds by a process similar to the two-dimensional (2-D) nucleation, it is well known that the twin-plane re-entrant edge created by the (111) double twin provides sites for easier growth, as reported in previous studies on $BaTiO_3$[10–14] and other systems.[15,16] This mechanism has been known

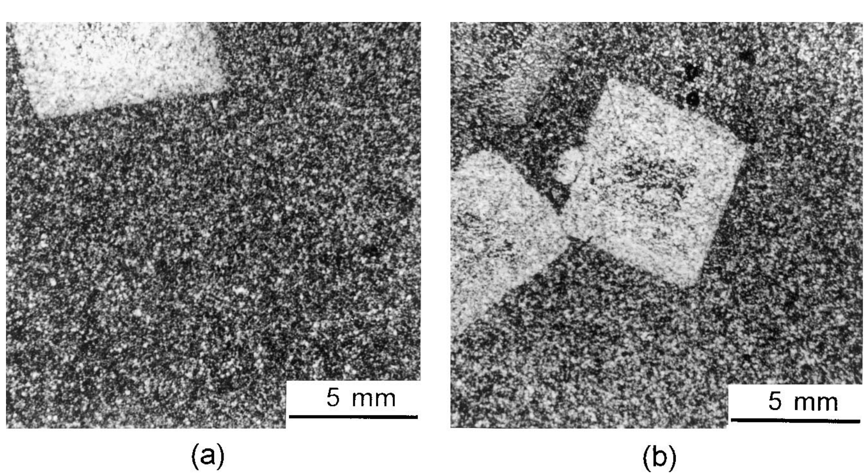

Fig. 2. Microstructures of $BaTiO_3$ specimens sintered at 1365°C for (a) 1 h and (b) 3 h. They were further heat-treated at 1355°C for 20 h.

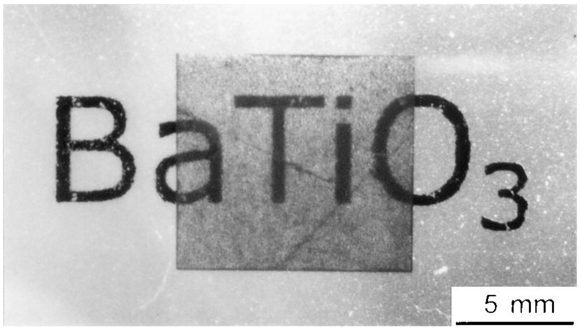

Fig. 4. Optical quality of $BaTiO_3$ single crystal cut from the specimen shown in Fig. 3.

as the twin-plane re-entrant edge (TPRE) growth mechanism.[17,18] During the SAGG, the material transfer occurred preferentially to the grains with a (111) double twin and thus some grains containing a (111) double twin grew much faster than the other grains without it. Therefore the growth of single crystals proceeded by the TPRE growth mechanism.

In summary, a simple method for growing $BaTiO_3$ single crystals has been developed, which consists of a two step heat-treatment process. The first heat-treatment at 1365°C for 1 h is to allow the nucleation of a limited number of secondary abnormal grains and the second one at 1355°C is to allow them to grow without further nucleation. Single crystals larger than 1×1 cm were easily obtained.

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