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Single crystal growth of $BaTiO_3$ by sintering

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$BaTiO_3$ single crystals are fabricated through sintering from seeded polycrystals. The condition for single crystal growth is essentially dependent on the grain growth behavior of polycrystalline sintered bodies. The $BaTiO_3$ sinters with a small excess TiO_2 is suitable for obtaining large single crystals. Single crystals with $3x3x0.5mm^3$ in size is obtained for Ti-excess $BaTiO_3$ in solid state.

1. INTRODUCTION

Fabrication of $BaTiO_3$ single crystals has long been examined since $BaTiO_3$ was discovered. However, the transformation point from hexagonal to cubic phase at 1460°C makes difficult to fabricate $BaTiO_3$ single crystals from stoichiometric melts [1]. Proeutectic reaction is used to avoid the transformation point for the growth of single crystals such as flux method [2], FZ method [3] and Top Seeded Solution Growth (TSSG) method [4].

A very different method using abnormal grain growth of sinters in solid state has successfully been applied to prepare single crystals of Mn-Zn ferrite [5]. We have reported that this method can be used to get single crystals of $BaTiO_3$ with a small excess of TiO_2, which exhibits abnormal grain growth at high temperatures [6].

This paper aims to report the influence of Ba/Ti ratio on the grain growth of $BaTiO_3$ and to show the condition for single crystal in solid state.

2. EXPERIMENTAL PROCEDURE

The raw material used is high-purity(99.9%) and fine-grained (0.2μm) commercial $BaTiO_3$ powders (Sakaikagaku Inc., Japan) fabricated through hydro-thermal method. The Ba/Ti ratio of powders was estimated to be 0.998 by means of X-ray fluorescence analysis (XFA) within the accuracy of the level 0.001. The samples with Ba/Ti ratio of 0.999, 1.000 and 1.001 were fabricated from original powders and a dilute solution of $Ba(CH_3COO)_2$ with H_2O. In this report, sintered bodies with Ba/Ti ratio of 0.999, 1.000 and 1.001 are noted as Ti-excess, stoichiometric and Ba-excess compounds. Dried and sieved powders were uniaxially pressed at 1.5MPa with a cemented carbide die into a square bar of $5x5x25mm^3$ in size, and further isostatically pressed under a pressure of 150MPa. The green compacts were sintered at 1250°C for 10h without any sintering aids. Relative density obtained is 98.6% for Ti-excess, 99.1% for stoichiometric and 97.8% for Ba-excess compounds, respectively. Cube samples of $3x3x3mm^3$ in size were machined from the sintered bodies. The grain growth behavior was investigated in a temperature range between 1280°C and 1340°C.

Single crystal seeds were fabricated through Remeika method [2] using reagent grade KF powders as a flux. For single crystal growth, the seed crystal was contacted with a polycrystalline sample. A (001) surface of the seed crystal was used for contact plane. The surfaces of seed and polycrystalline substrate for contact were carefully ground, polished and finished with 0.25μm diamond paste. They were joined under a pressure of 1.5MPa at 1200°C for 2h.

Microstructures were examined with optical microscope (OM, NIKON OPTIPHOTO) and scanning electron microscope (SEM, JEOL JSM-5200). The samples were thermally etched or chemically-etched with a mixture of dilute HCl solution containing a small amount of HF.

2. RESULTS & DISCUSSION

The grain growth of $BaTiO_3$ is vitally affected by a small change of Ba/Ti ratio. Fig. 1 shows the microstructures of each compound in as-sintered state. The grain size is about 2.7μm, 5.6μm and 8.3μm in Ti–excess, stoichiometric and Ba–excess compounds respectively. Ba–excess compound has larger grain size than other two compounds.

The grain growth in Ti–excess and stoichiometric compounds was found to be very unique. Fig. 2 is the etched sections of Ti–excess compound annealed at 1280°C (a) and at 1340°C (b) for 0.5h, respectively. Several coarse grains are generated in fine–grained matrix as shown in Fig. 1(a), while fine grains no longer exist and the average grain size becomes very large by annealing at 1340°C. The difference in grain size is very marked, i.e., 2.6μm in (a) and 250μm in (b). In the stoichiometric compound, the grain growth behavior is similar to that of Ti–excess compound. The stoichiometric compound may have a small excess of TiO_2, which is less than the limit of XFA analysys. The grain growth behavior of Ti–excess and stoichiometric compounds is regarded as abnormal grain growth. In contrast, the grain size increases gradually with an increase of annealing temperature in Ba–excess compound as demonstrated in Fig. 3. In this compound, the grain size distribution is uniform

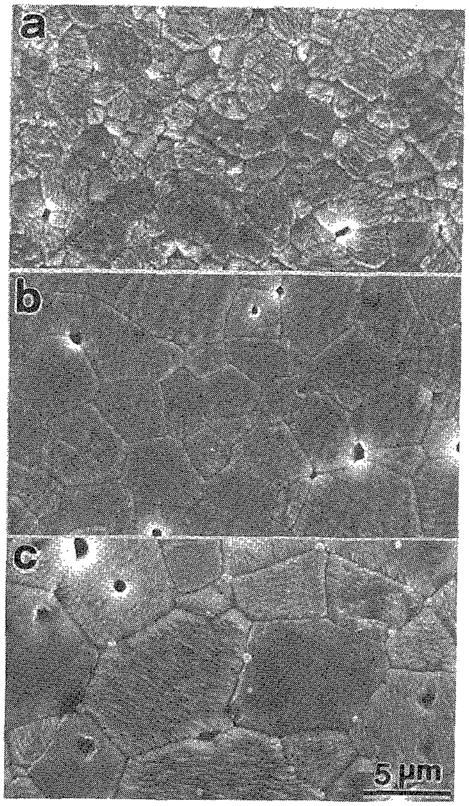

Figure 1. Thermal etched sections of sintered bodies, (a) Ti–excess, (b) stoichiometric and (c) Ba–excess compounds.

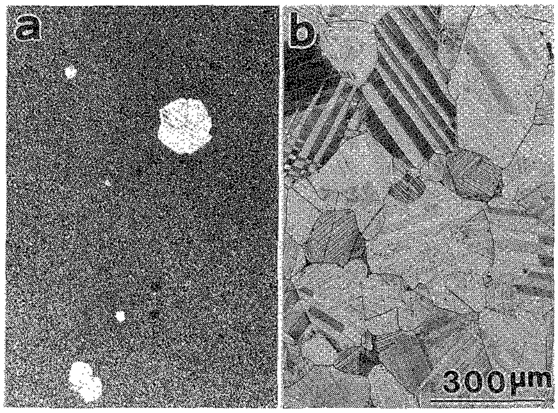

Figure 2. Optical micrographs of Ti–excess compound annealed for 0.5h, (a) at 1280°C and (b) at 1340°C.

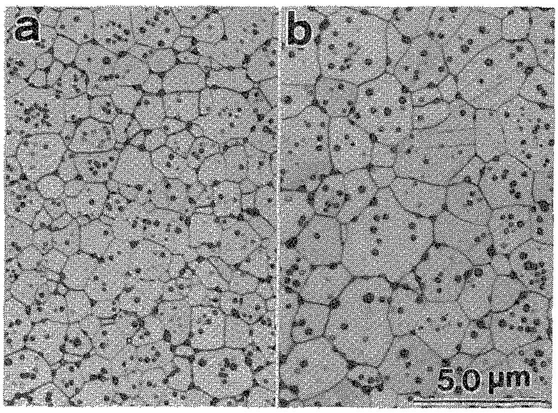

Figure 3. Etched sections of Ba–excess compound annealed for 0.5h, (a) at 1280°C and (b) at 1340°C.

at all temperatures examined. The average grain size is 13.6μm at 1280°C (Fig. 3(a)), and 22.5μm at 1340°C (Fig. 3(b)).

Fig. 4 is a plot of average grain size against isochronal annealing temperature. The grain growth behavior is very different between Ba-excess and other two compounds. In Ba-excess compound, the average grain size gradually becomes larger at higher annealing temperature. This is typical of materials exhibiting normal grain growth. On the contrary, the average grain size abruptly changes at around 1330°C in Ti-excess compound and at around 1320°C in stoichiometric one. In the two compounds, the grain growth is extremely sluggish below the critical temperature. The sluggish grain growth may be responsible for abnormal grain growth in the two materials. The grain size difference above and below the critical temperatures is very large e.g. the average grain size of Ti-excess compound is 7.8μm at 1320°C and is 250μm at 1340°C respectively. Since the grain growth behavior of stoichiometric compound is similar to Ti-excess compound, this material may have a small excess of Ti, which is less than 0.001.

Single crystal growth in solid state depends on the grain growth behavior of sinters. The material exhibiting abnormal grain growth is suitable for single crystal growth. Fig. 5 is the cross section of the seeded Ba-excess sample annealed at 1300°C for 10h. The migration of the interface from the seed crystal to the substrate is very limited. Ba-excess compound exhibits normal grain growth, and the single crystal growth is very slow at the annealing temperature. In order to obtain a larger single crystal, Ti-excess compound, which exhibits abnormal grain growth, must be used. It was found that the migration of the interface between seed crystal and polycrystalline substrate is inhibited by the generation of coarse grains in substrate. Therefore, the annealing temperature must be chosen below the critical temperature of abnormal grain growth, i.e., below about 1320°C in the Ti-excess compound. The situation resembles that in Mn-Zn ferrite [5].

Fig. 6 shows an optical micrograph of seeded

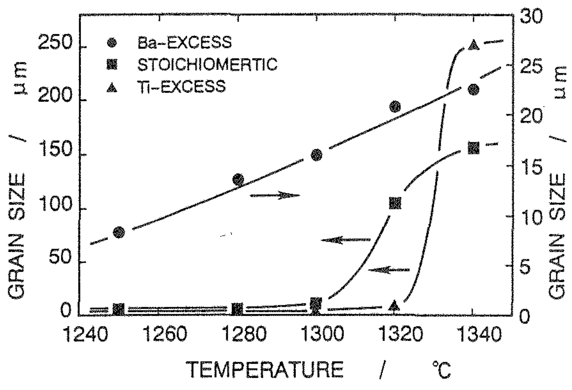

Figure 4. A plot of average grain size of each compound annealed for 0.5h at various temperatures.

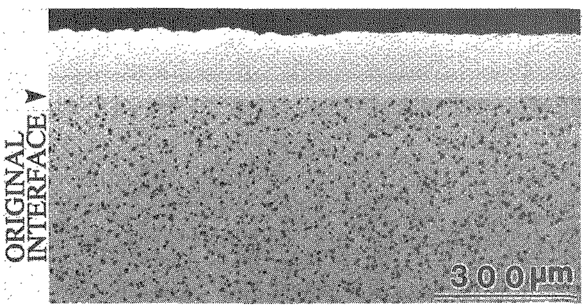

Figure 5. A cross section of seeded Ba-excess sample annealed at 1300°C for 10h. The single crystal seed (upper) was joined with polycrystalline substrate (lower) at the original interface. Note that the single crystal growth is almost negligible after the annealing.

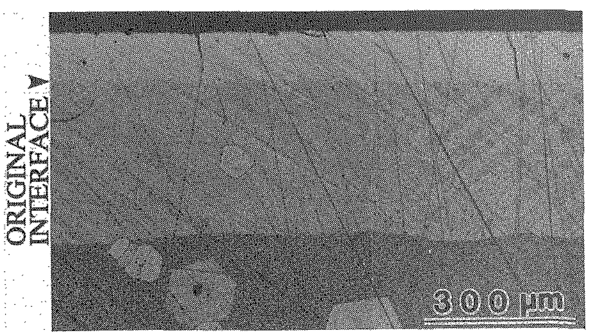

Figure 6. Etched section of seeded Ti-excess sample annealed at 1300°C for 1h.

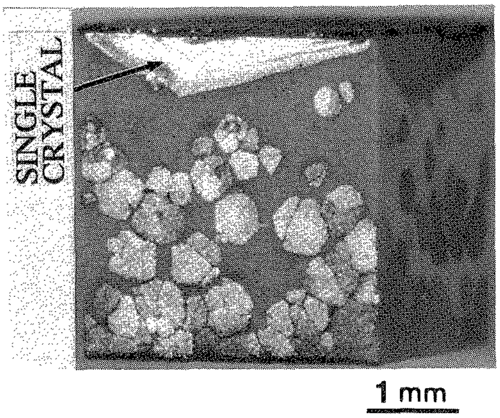

Figure 7. Seeded Ti-excess sample annealed at 1300°C for 30h.

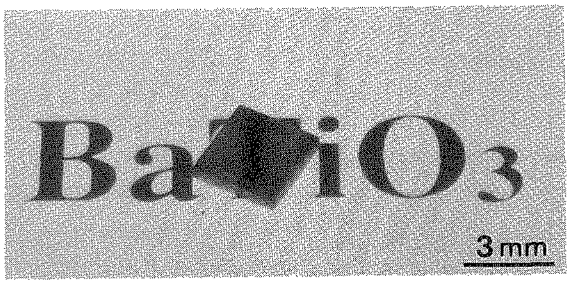

Figure 8. $BaTiO_3$ single crystal with $3x3x0.5mm^3$ in size.

Ti-excess sample annealed at 1300°C for 1h. The growth distance reaches up to 300μm. The result is very different from that in Ba-excess compound. Coarse grains are developed in fine grained matrix even at 1300°C and some coarse grains are included in the single crystal to form island crystals.

Fig. 7 is a whole view of the seeded Ti-excess compound annealed at 1300°C for 30h. The single crystal grows from the top of the sample to downward. The growth front of the single crystal appears nearly straight on the two side faces. This fact means that the single crystal grows to have a habit plane. The generation of planar interface is not favorable for further growth of single crystal. The habit plane could not definitely be determined with X-ray Laue analysis, but the traces of the planar growth front fall close to the {012} poles.

Fig. 8 shows the single crystal obtained. The size of the crystal is about $3x3x0.5mm^3$. The broad faces consist of (001) plane. The single crystal is not fully transparent but translucent due to the presence of some island crystals and residual pores. In order to obtain single crystals with higher quality, several conditions must be improved. First of all, high-purity powders with a controlled stoichiometry must be prepared with a sophisticated process. It is also important to find suitable sintering conditions to get fully dense and fine-grained sinter of $BaTiO_3$. In addition, the critical temperature for abnormal grain growth must be kept as high as possible, which may be controlled by nonstoichiometry.

4. CONCLUSIONS

The single crystal growth of seeded $BaTiO_3$ sinters with various Ba/Ti ratio is examined. The results obtained are summarized as follows,

1. $BaTiO_3$ with a small excess TiO_2 which exhibits abnormal grain growth is suitable for single crystal growth.
2. In order to obtain a large single crystal, the annealing temperature must be chosen just below the critical temperature of abnormal grain growth.
3. The single crystal with $3x3x0.5mm^3$in size is obtained in solid state.

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