

**Final Report for Korea – AFOSR Nanoscience and Technology Initiative
(AOARD-04-4052)**

**Control of Interface Structure for the
Development of Nanostructured Materials**

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14. ABSTRACT In this investigation, it was shown that the oxygen partial pressure affects considerably the grain boundary structure (morphology) of BaTiO3, a model oxide, and further the grain growth behaviour. There was a close correlation between the boundary structure and grain growth behaviour. It was possible, for the first time, to prepare different types of microstructures by properly controlling the oxygen partial pressure. This investigation also showed that with grain growth above a eutectic temperature, dry grain boundaries become wet due to the accumulation of solutes and the thickness of liquid films formed at the boundaries increases. Quantification of boundary structure and the chemical analysis of boundary segregation should be needed in subsequent investigations in order to provide more conclusive data for the new findings.					
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I. Introduction.

The properties of many ceramic materials are controlled primarily by their grain boundaries rather than by the bulk material itself. Control of grain growth is therefore a key requirement necessary for the preparation of high quality ceramics. Often, a fine grain size is required to achieve the optimum properties and recently much research has been carried out around the world in the fabrication of nanoceramics with a grain size < 100nm. These nanoceramics offer the possibility of improved mechanical and electrical properties. However, grain growth is a key issue. Since the driving force for grain growth is inversely proportional to grain size, fast grain growth (often exhibiting abnormal grain growth) occurs in nanopowders, negating their benefit.

During sintering, both densification and grain growth occur. In order to suppress fast grain growth, various techniques based on low temperature processing and external pressure application have been proposed and developed. The basic ideas for these techniques reside in the reduction of thermal energy that promotes grain boundary migration and grain growth. Another way of suppressing fast grain growth is by altering the boundary structure. Changes in boundary structure have a considerable effect on grain growth behaviour and allow control of grain growth using conventional sintering techniques. Control of the boundary structure is of importance for materials ranging from nanomaterials to single crystalline. However, the key factors that govern the relationship between boundary structure and grain growth and related fundamental principles are as yet unclear. It is therefore crucial to study the basic principles of grain growth control and their application to producing ceramic materials. In particular, the effect of boundary structure on grain growth and densification in sub-micron and nanostructured materials have yet to be studied. We have carried out original and unique research in this area.

II. Achievements. (AOARD-04-4052)

Over the last 12 months we have looked at the effect of oxygen partial pressure on grain boundary structure and grain growth in BaTiO_3 . In our previous work we found that the microstructure of BaTiO_3 sintered below the eutectic temperature depended strongly on the sintering atmosphere [1-4]. In an oxidising atmosphere, the grain boundaries were faceted and grain growth was either suppressed or abnormal grain

growth occurred. In an oxidising atmosphere abnormal grain growth was dependant on the presence of (111) twins. In a strongly reducing atmosphere, the grain boundaries were rough and normal grain growth occurred. (111) twins were also absent.

In our recent work, we found that abnormal grain growth can occur in reducing atmospheres even when (111) twins were absent. Figure 1 shows SEM micrographs of 0.1 mol % TiO_2 excess BaTiO_3 sintered at 1250°C for 50 hours in increasingly reducing atmospheres. In the weakly reducing atmosphere, all grain growth is suppressed [Fig. 1 (a)]. In the strongly reducing atmosphere, normal grain growth takes place [Fig. 1 (d)]. In the moderately reducing atmospheres, abnormal grain growth takes place without the presence of (111) twins [Figs. 1 (b) and (c)].

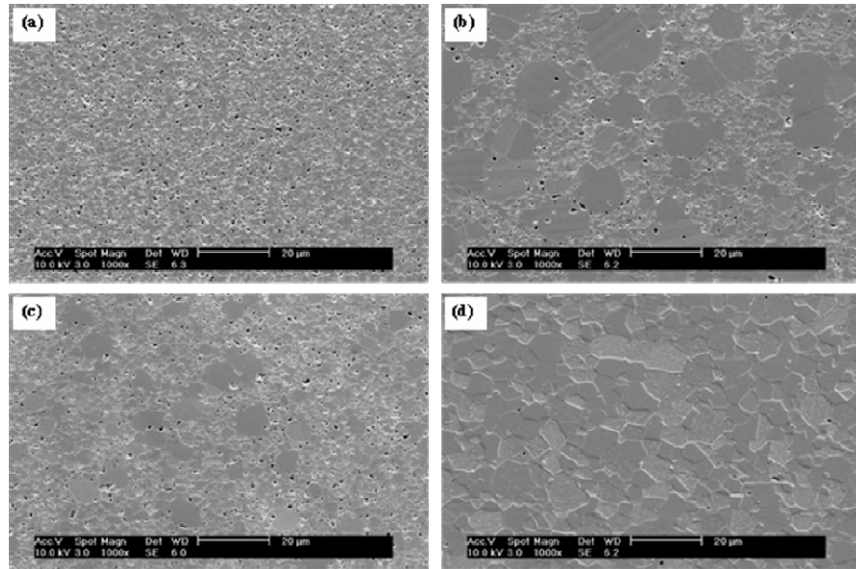


Fig. 1. Microstructures of 0.1mol%- TiO_2 -excess BaTiO_3 sintered at 1250°C for 50h in oxygen partial pressure of (a) $\sim 2 \times 10^{-17}$ atm, (b) $\sim 8 \times 10^{-18}$ atm, (c) $\sim 4 \times 10^{-18}$ atm, and (d) $\sim 4 \times 10^{-19}$ atm, respectively.

This abnormal grain growth is caused by the presence of partially faceted / partially rough grain boundaries. In the samples sintered in an oxidising or weakly reducing atmosphere, the grain boundaries are faceted [Fig. 2 (a)]. The driving force necessary for grain boundary movement is very high and grain growth is suppressed. In the moderately reducing atmosphere, the grain boundaries are partially faceted and partially rough [Fig. 2 (b)]. The driving force necessary for grain boundary movement is reduced and so some grains can grow, resulting in abnormal grain growth. In the strongly reducing atmosphere, the grain boundaries are completely rough [Fig. 2 (c)]. The driving force necessary for grain boundary movement is low and so all grains can

grow, resulting in normal growth.



Fig. 2. TEM microstructures of 0.1mol%-TiO₂-excess BaTiO₃ sintered at 1250°C for 50h in (a) air, (b) mixed gases (80N₂-20H₂), and (c) H₂, respectively.

We have also been looking at the formation and thickening of intergranular amorphous films at grain boundaries in BaTiO₃ [5]. The presence of an amorphous film between grains is important not only for grain growth, but also for mechanical and electrical properties of the ceramic. In experiments involving BaTiO₃ single crystals embedded into a matrix of 0.4 mol % TiO₂ excess BaTiO₃ powder, it was shown that an amorphous film formed and thickened at the single crystal boundary as it grew into the matrix [Fig. 3]. The film was formed by the accumulation of segregated solutes at the single crystal boundary and the redistribution of pockets of liquid located at triple junctions between the matrix grains.

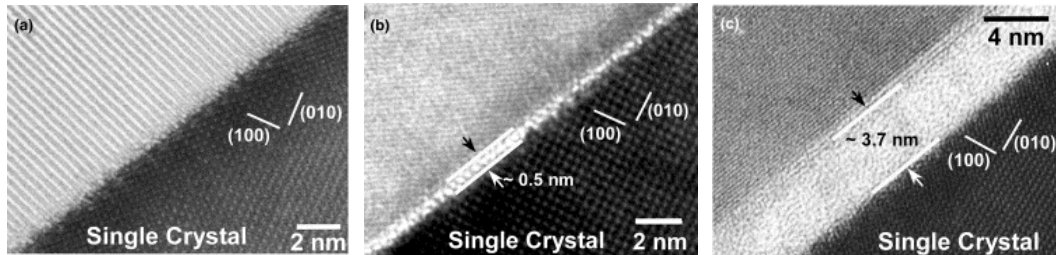


Fig. 3. HREM images of the boundaries between a (1 0 0) single crystal and a fine matrix grain. Single crystal/polycrystal bi-layer samples with 0.4-mol%-TiO₂ addition annealed at 1350°C for (a) 5, (b) 20 and (c) 50 h in air after H₂-treatment at 1250°C for 10 h

III. Conclusions.

In this investigation, we showed that the oxygen partial pressure affects considerably the grain boundary structure (morphology) of BaTiO₃, a model oxide, and

further the grain growth behaviour. There was a close correlation between the boundary structure and grain growth behaviour. It was possible, for the first time, to prepare different types of microstructures by properly controlling the oxygen partial pressure.

This investigation also showed that with grain growth above a eutectic temperature, dry grain boundaries become wet due to the accumulation of solutes and the thickness of liquid films formed at the boundaries increases.

Quantification of boundary structure and the chemical analysis of boundary segregation should be needed in subsequent investigations in order to provide more conclusive data for the new findings.

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