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Atomic-level structure of a Ti-rich intergranular layer in $BaTiO_3$ ceramics revealed by STEM

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$BaTiO_3$-based ceramics are a model system for studying abnormal grain growth (AGG). For AGG to occur, excess Ti is required, and it is generally considered that the excess Ti bonds at grain boundaries (GBs) are a key to understanding the AGG behavior [1-4]. Unfortunately, the bonding at GBs in Ti- excess $BaTiO_3$-based ceramics is not well understood. Here we report the atomic-level structure of an intergranular layer in a $BaTiO_3$-based ceramic characterized by scanning transmission electron microscopy (STEM).

Er-doped Ti-excess $BaTiO_3$ ($BaEr_{0.002}Ti_{1.004}O_3$) was prepared by the conventional solid-state reaction method, with the final sintering performed at 1300ºC for 10 h. A Cs-corrected JEM-2100F was used for HAADF-STEM imaging (detection angle range: 73-194 spatial mrad).

Abnormally-grown large grains with polyhedral shape were observed as shown in fig. 1(a), confirming that AGG occurred during sintering. After further TEM observation, it was found that both matrix GBs (boundaries between matrix grains, fig. 1(b)) and abnormal GBs (boundaries between abnormal grains and neighboring matrix grains, fig. 1(c)) were asymmetric with a (111) habit plane on one side of the boundary, which is a characteristic of GBs in AGG $BaTiO_3$-based ceramics [3-4]. Using HAADF-STEM, an intergranular layer was identified at such GBs. For example, in figure 1(d) the intergranular layer, which has an epitaxial relationship with the (111) plane of the abnormal grain, is clearly visible. It was also found that the intergranular layer continued to triple junctions, and at some triple junctions the intergranular phase transited completely into the Ti-rich $Ba_4Ti_{12}O_{27}$ phase. The intergranular layer can be described as a $Ba_4Ti_{12}O_{27}$-like phase with half the *a* lattice parameter of $Ba_4Ti_{12}O_{27}$. This is shown more clearly in fig. 1(e), which is an enlarged image of the dashed rectangle region in fig. 1(d). Model structures of $BaTiO_3$ $[1\bar{1}0]$ and $Ba_4Ti_{12}O_{27}$ $[0\bar{1}0]$ are superimposed on the image in accordance with the epitaxial relationship. Thus the GB layer can be seen to share a common Ti plane with the abnormal grain, indicated by a dashed line in Fig. 1(e). It is worth pointing out that the Ti-rich intergranular layer can accommodate the excess Ti and form at all the GBs with $BaTiO_3$ {111} habit planes. The intergranular layer should thus preferentially form GBs with {111} habit planes, which are necessary for AGG to occur.

This study clearly shows an intergranular layer with $Ba_4Ti_{12}O_{27}$-like structure at GBs with {111} habit planes in AGG $BaTiO_3$-based ceramics. Further investigations are being carried out.

References

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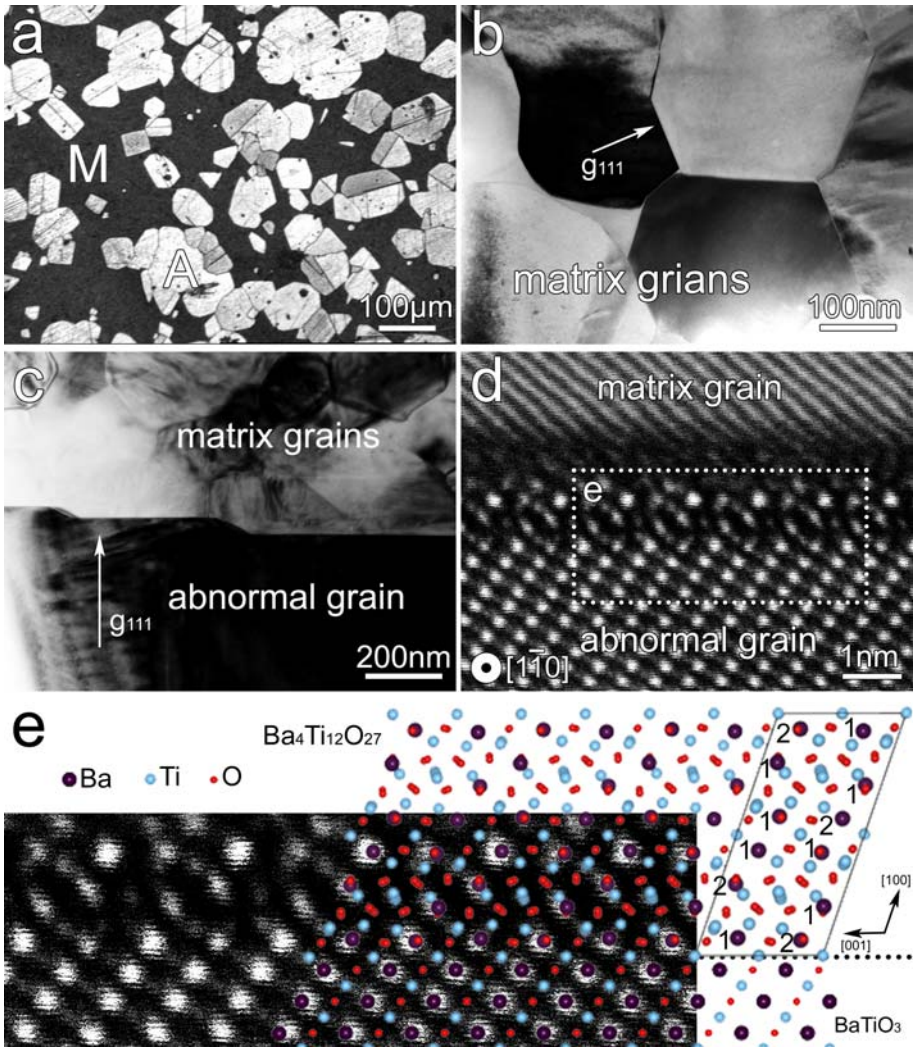

Figure 1: (a) an optical micrograph showing matrix and abnormal grains marked M and A respectively; (b) and (c) Bright-field images showing typical GBs with {111} habit planes for a matrix GB and an abnormal GB respectively; (d) a typical HAADF-STEM image of an abnormal GB showing the intergranular layer; (e) an enlarged HAADF-STEM image of the dashed rectangle region superimposed with the model structure. In (e) a unit cell projection of $Ba_4Ti_{12}O_{27}$ is indicated by a gray line, two kinds of Ba columns with different atom densities in the projection direction are indicated by numbers 1 and 2. The shared Ti plane at the interface is indicated by a dashed line.