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Effect of Al_2O_3 dopant on abnormal grain growth in $BaTiO_3$

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Abstract

The effect of additions of up to 1 mol% Al_2O_3 on abnormal grain growth in $BaTiO_3$ has been studied. For samples sintered at temperatures $\leq$1250 °C addition of 0.1 mol% Al_2O_3 increases the number density of abnormal grains, with further additions reducing the number density. For samples sintered at 1350 °C, addition of Al_2O_3 caused the primary abnormal grain size to decrease and then increase. The results are explained by considering the effect of Al_2O_3 addition on the TiO_2 content of grain boundaries.

Keywords: Grain boundaries; Al_2O_3; $BaTiO_3$ and titanates; Abnormal grain growth; Perovskites

1. Introduction

$BaTiO_3$ is an important dielectric ceramic with many uses such as capacitors and positive temperature coefficient of resistance materials. In these applications, microstructure control is vital. Abnormal grain growth (AGG) should be avoided as it has a detrimental effect on mechanical and electrical properties.[1] AGG is affected by dopants, which form a liquid phase during sintering.[2]

When $BaTiO_3$ is donor-doped, its electrical behaviour changes from insulating to semiconducting, with a sharp increase in resistivity at the Curie point.[3] However, when the donor concentration exceeds 0.5 at.%, $BaTiO_3$ becomes insulating again and the grain size decreases dramatically. This is known as the grain growth anomaly[4] and has been studied extensively.[4,5] The effect of acceptor dopants on the grain growth of $BaTiO_3$ is less well known. Acceptor dopants are often present as impurities and are sometimes added as sintering aids.[6–8] Both Na_2O and CaO inhibit abnormal grain growth.[9,10] In the present paper, the effect of Al_2O_3 additions of up to 1 mol% on the abnormal grain growth behaviour of $BaTiO_3$ will be described.

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2. Experimental

$BaTiO_3$ powders were prepared from Fuji Titanium HPBT-1 $BaTiO_3$ (99.8 wt.% purity, 0.66 μm size) and Sumitomo AKP-50 Al_2O_3 (>99.99 wt.% purity, 0.1–0.3 μm size). The Ba/Ti ratio of the $BaTiO_3$ powder is 0.996, i.e. there is a slight TiO_2 excess. Powders were prepared with additions of 0, 0.1, 0.2, 0.5 and 1.0 mol% Al_2O_3. The powders were ball milled in ethanol in polypropylene jars using ZrO_2 milling media. After milling, the slurries were dried, crushed and passed through a 150-μm sieve. Samples 9 mm in diameter and 4 mm thick were prepared by cold isostatic pressing at 200 MPa. Samples were placed on $BaTiO_3$ spacers in an alumina crucible and sintered in an alumina tube furnace. Samples were sintered at 1200, 1250, 1300 and 1350 °C. The sintering time for the samples sintered at 1200 and 1250 °C was 100 h. The sintering time for the samples sintered at 1300 and 1350 °C was 1 h.

Samples for optical microscopy and scanning electron microscopy were sectioned, polished to a 0.25-μm finish and etched in a 1% HF–4% HCl solution for ~5 s. Abnormal grain number density was measured from optical micrographs. The 2D primary abnormal grain size was measured using an image analyzing program (Matrox Inspector) and divided by 0.76 to determine the 3D grain size.[11] Samples for SEM were gold

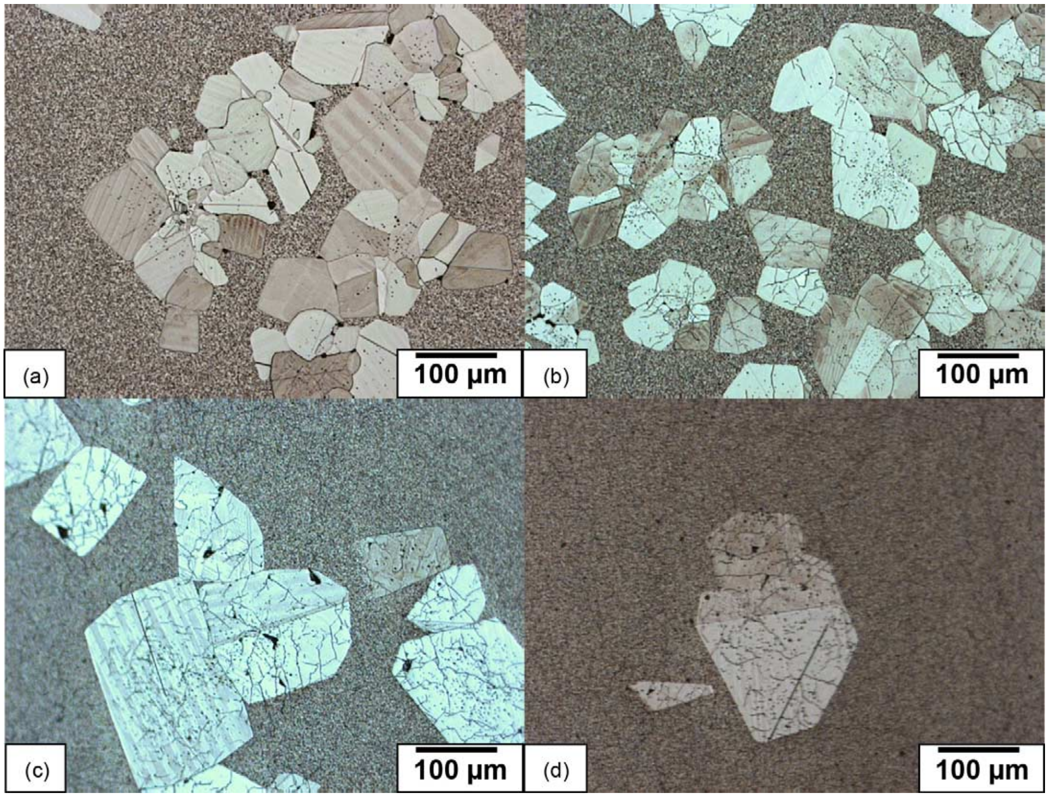

Fig. 1. BaTiO3 samples doped with: (a) 0; (b) 0.1; (c) 0.5 and (d) 1.0 mol% Al_2O_3 sintered at 1250 °C for 100 h.

coated and viewed in a Model XL 30 S FEG SEM (Philips, Eindhoven, Netherlands). Samples were also prepared for wavelength dispersive spectroscopy (WDS). Samples were polished and etched as above, carbon coated, and viewed in a Model 515 SEM (Philips, Eindhoven, Netherlands).

3. Results

Optical micrographs of samples sintered at 1250 °C for 100 h are shown in Fig. 1. The microstructures are bimodal, with fine matrix grains and faceted abnormal grains. Addition of 0.1 mol% Al_2O_3 causes an increase in the number of abnormal grains, with further additions causing a decrease. At an addition of 1 mol% Al_2O_3, abnormal grain growth is almost entirely absent.

Optical micrographs of samples sintered at 1350 °C for 1 h are shown in Fig. 2. In all the samples primary abnormal grain growth (PAGG) has taken place, the fine matrix grains having been completely consumed by coarse primary abnormal grains (PAG). Addition of Al_2O_3 up to 0.5 mol% causes a reduction in PAG size. Further addition of Al_2O_3 causes an increase in PAG size.

The effect of Al_2O_3 addition on the number density of abnormal grains is shown in Fig. 3. For samples sintered at 1200 and 1250 °C, addition of 0.1 mol% Al_2O_3 causes a large increase in the number density of abnormal grains. Further additions cause a sharp decrease in the number density of abnormal grains. At additions of 1 mol% Al_2O_3, abnormal grain growth has almost ceased.

For samples sintered at 1300 and 1350 °C, abnormal grain number density increases with Al_2O_3 content and then de-

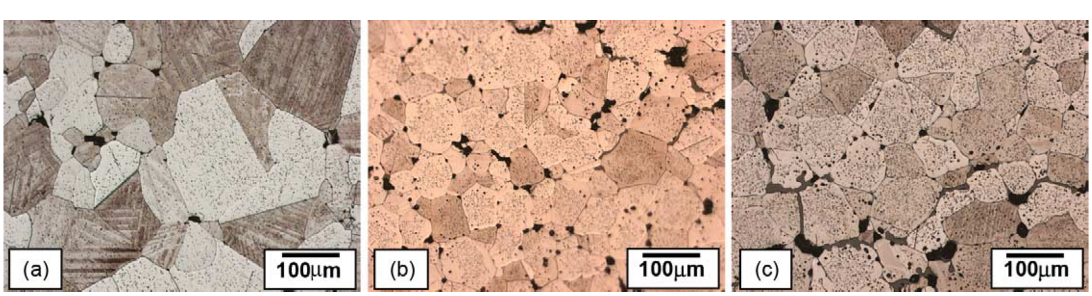

Fig. 2. BaTiO3 samples doped with: (a) 0; (b) 0.5 and (c) 1.0 mol% Al_2O_3 sintered at 1350 °C for 1 h.

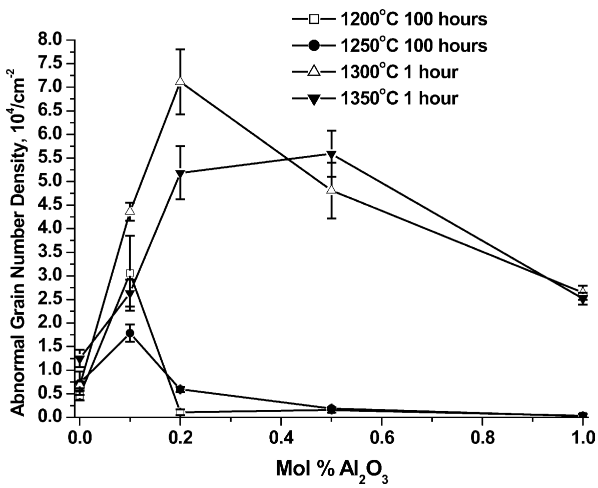

Fig. 3. Effect of Al_2O_3 addition on abnormal grain number density.

creases gradually. As the sintering temperature increases, the point at which abnormal grain number density reaches its maximum value shifts to higher Al_2O_3 contents (0.2 mol% Al_2O_3 for samples sintered at 1300 °C, 0.5 mol% Al_2O_3 for samples sintered at 1350 °C). In the samples sintered at 1300 °C, although the number density of abnormal grains decreases with addition of more than 0.2 mol% Al_2O_3, the size of the abnormal grains continues to increase. The samples containing 0.5 and 1.0 mol% Al_2O_3 show almost complete PAGG. It should be noted that, technically speaking, the samples sintered at 1350 °C display normal grain growth, as the original fine grained matrix has been completely consumed by PAGG to form a normal distribution of coarse grains. However, for the sake of comparison, in this paper they shall be considered to be abnormal grains.

SEM micrographs of samples containing 0.5 mol% Al_2O_3 sintered at 1200 °C for 100 h and 1350 °C for 1 h are shown in Fig. 4. The sample sintered at 1200 °C contains precipitates both in the abnormal grains and in the matrix. WDS of these precipitates gives them the composition $Ba_4Al_2Ti_{10}O_{27}$. This precipitate is present in the samples with more than 0.1 mol% of Al_2O_3 sintered at 1200 and 1250 °C. The sample sintered at 1350 °C for 1 h has faceted solid/liquid interfaces between the primary abnormal grains. As Al_2O_3 is added, an amorphous phase builds up at the solid/liquid interfaces and at triple junctions (marked with arrows). In the sample with 1 mol% Al_2O_3 this phase has almost completely penetrated the solid/liquid interfaces. All of the samples show faceted grain boundaries or solid/liquid interfaces, regardless of Al_2O_3 content or sintering temperature.

4. Discussion

The samples can be separated into two groups: samples sintered at temperatures ≤1250 °C and samples sintered at temperatures ≥1300 °C. In the samples sintered at temperatures ≤1250 °C, Al_2O_3 is incorporated into the $BaTiO_3$ lattice by substitution for TiO_2. TiO_2 leaves the $BaTiO_3$ lattice and segregates at the grain boundaries. Excess TiO_2 is known to promote abnormal grain growth in $BaTiO_3$ temperatures ≤1250 °C.[12,13] In the sample with 0.1 mol% Al_2O_3, the Al_2O_3 is completely incorporated into the $BaTiO_3$ lattice. This causes segregation of TiO_2 at the grain boundaries and promotes abnormal grain growth. In samples with more than 0.1 mol% Al_2O_3, $Ba_4Al_2Ti_{10}O_{27}$ precipitate formation removes TiO_2 from the grain boundaries, leading to a decrease in the number of abnormal grains. Similar behaviour occurs in $BaTiO_3$ doped with Na_2O.[9] Abnormal grain growth could also be caused by inhomogeneities in the green compact microstructure such as agglomerate formation. However, such inhomogeneities should lead to a random abnormal grain growth behaviour with varying Al_2O_3 content, whereas our samples showed a definite pattern.

In the samples sintered at temperatures ≥1300 °C, Al_2O_3 dissolves in the $BaTiO_3$ lattice as above, releasing TiO_2. The excess TiO_2 reacts with un-dissolved Al_2O_3 and impurities to create a liquid film between the grains. The eutectic point in the $BaTiO_3$ system can be lowered to ∼1250 °C by the addition of Al_2O_3–SiO_2–TiO_2.[14] This liquid film can promote primary abnormal grain growth at temperatures lower than 1332 °C.[15] As the amount of Al_2O_3 increases, the volume

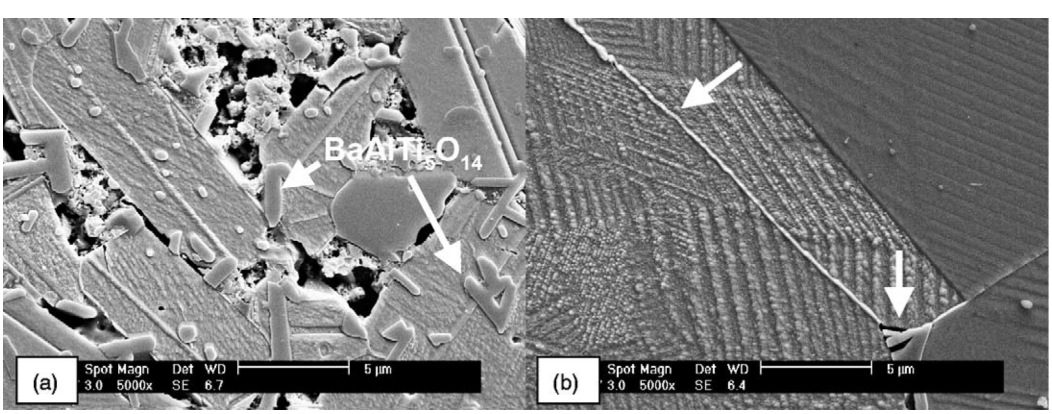

Fig. 4. (a) 0.5 mol% Al_2O_3, 1200 °C, 100 h; (b) 0.5 mol% Al_2O_3, 1350 °C, 1 h.

of liquid film at the interfaces increases. This liquid film is expected to reduce the growth rate of the primary abnormal grains, leading to a reduction in PAG size. Such behaviour has been noted in Ca-doped $BaTiO_3$.[10] In the Al_2O_3-doped samples, addition of up to 0.5 mol% Al_2O_3 causes a reduction in PAG size, but further addition of Al_2O_3 causes an increase. The reason for this is not yet clear but may be due to secondary abnormal grain growth. Addition of SiO_2 to $BaTiO_3$ is known to induce secondary abnormal grain growth.[16] Further, sintering experiments are being carried out to see if this is the case.

5. Conclusions

$BaTiO_3$ has been doped with up to 1 mol% Al_2O_3 and sintered at various temperatures. For samples sintered at temperatures $\leq$1250 °C, addition of up to 0.1 mol% Al_2O_3 promotes abnormal grain growth, with further additions of Al_2O_3 inhibiting it. AGG promotion is caused by Al_2O_3 dissolving in the $BaTiO_3$ lattice and releasing TiO_2. AGG inhibition occurs by Al_2O_3 reacting with excess TiO_2 and $BaTiO_3$ to form $Ba_4Al_2Ti_{10}O_{27}$. For samples sintered at temperatures $\geq$1250 °C, Al_2O_3 reacts with excess TiO_2 and impurities to form a thick liquid film at the grain boundaries. As the Al_2O_3 content increases, the volume of the liquid film increases, retarding grain growth. However addition of 1 mol% Al_2O_3 causes grain growth to increase. This may be due to secondary abnormal grain growth.

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