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The effect of $TiCl_3$ on the microstructure of donor-doped boron-added Ti-excess $BaTiO_3$

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Abstract

The effect of $TiCl_3$ and 0.5, 1.0, 2.0 mol% B_2O_3 addition on the microstructure and on the densification of Ti-excess $BaTiO_3$ were investigated. Sb_2O_3 was used as a donor dopant in boron containing compositions. The Ti-excess, platelet-type $Ba_2Ti_5O_{12}$ or $Ba_4Ti_{12}O_{27}$ phases were detected in undoped and Ti-excess formulations and compositions doped with 0.5 mol% B_2O_3, which were sintered below the eutectic temperature. Suppression of these platelet-type grains occurred in the formulations containing more than 0.5 mol% B_2O_3. Donor doping by Sb_2O_3 was very effective for promoting twin formation due to the increased concentration of the Ti^{3+} ions. Sudden grain growth occurred at the 2 mol% B_2O_3 addition level, with the loss of twin lamellae within the structure. The addition of 0.2 mol% excess TiO_2 in liquid form ($TiCl_3$) to the 0.5 mol% B_2O_3 containing sample, reduced the size and the number of polygonal grains and had a marked effect on the twin formation due to the homogeneous distribution of the excess Ti ions in the composition. The effects of adding the grain boundary modifier B_2O_3 (before and after the calcination step) on the microstructure and on the positive temperature coefficient of resistivity (PTCR) of Sb_2O_3 donor-doped Ti-excess barium titanate (BT) were also investigated; PTCR effects up to 5.0 orders of magnitude were obtained.

Keywords: Barium titanate; Sintering; Electrical properties; Grain growth; Thermistors

1. Introduction

The electric properties of the $BaTiO_3$ (BT) are dependent on the microstructure and chemical composition. Generally, optimisation of the electrical properties such as positive temperature coefficient of resistivity (PTCR) of $BaTiO_3$ requires a high density and controlled microstructure. At sintering temperatures below the eutectic, nearly all the large crystallites are found in the form of lamellae.[1] This process is accompanied by the growth of double twinned crystallites. Juggle[2] pointed out that in Ti-excess BT, the twins appear during grain growth and the number of twins is proportional to the concentration of Ti^{3+} ions. However Lee and Kang[3] reported that the (1 1 1) twin formation was affected by the particle size of the $BaTiO_3$ and the added excess TiO_2 powder.

Hence in this work, the effect of 0.5, 1.0 and 2.0 mol% B_2O_3 addition to the Ti-excess and Sb_2O_3 donor-doped BT compositions on the microstructure changes, PTCR characteristics, abnormal grain growth and on the twin formation in BT below the eutectic temperature were investigated. Furthermore the 0.2 mol% excess part of the TiO_2 in the 0.5 mol% B_2O_3–Sb_2O_3 containing composition was replaced with $TiCl_3$ in order to investigate the effect of chemical homogeneities on the twin formation. The further aim of this work was to elucidate the effect of the processing conditions for which the boron source was added to the BT compositions before and after the calcination step employed in the processing. Also, the PTCR characteristics of the boron-added BT ceramics were compared with the SiO_2-added BT, which is widely used as liquid phase sintering additives. Hence this study summarizes the work carried out as part of COST 525 project.[4–7]

2. Experimental procedure

The barium titanate (BT) compositions were prepared by the conventional ceramics processing techniques, which have been described in elsewhere.[4] The samples coded 21 and 51 were

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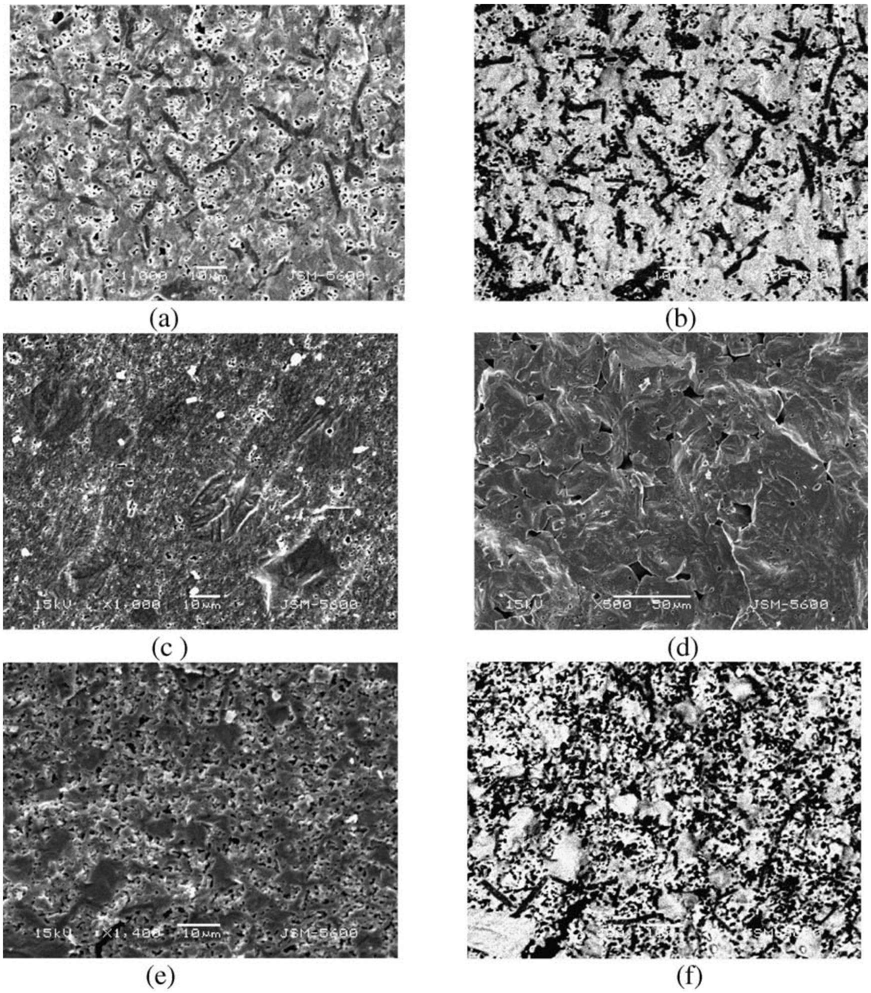


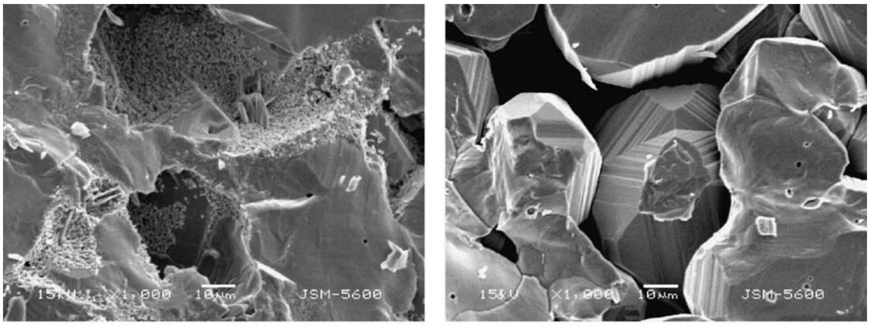
Fig. 1. The microstructures of stoichiometric and non-stoichiometric $BaTiO_3$ samples sintered at 1300 °C/1 h: (a) Ba-excess $BaTiO_3$. (b) Backscattered image of sample in (a). (c) Stoichiometric $BaTiO_3$. (d) $TiCl_3$-added stoichiometric $BaTiO_3$. (e) Ti-excess $BaTiO_3$. (f) Backscattered image of sample in (e).

prepared by the same method but 0.2 mol% TiO_2 was added in the form of $TiCl_3$. Water-soluble H_3BO_3 was used as the B_2O_3 source. The compositions prepared are given below.

Code	Compositions
1	$BaTi_{0.9975}O_3$
2	$BaTiO_3$
21	$BaTiO_3$ (0.2 mol TiO_2 added as $TiCl_3$)
3	$BaTi_{1.02}O_3$
4	$BaTi_{1.02}O_3$ + 0.25 mol% Sb_2O_3
5	$BaTi_{1.02}O_3$ + 0.25 mol% Sb_2O_3 + 0.5 mol% B_2O_3
51	$BaTi_{1.02}O_3$ (0.2 mol% excess TiO_2 added as $TiCl_3$) + 0.25 mol% Sb_2O_3 + 0.5 mol% B_2O_3
6	$BaTi_{1.02}O_3$ + 0.25 mol% Sb_2O_3 + 1.0 mol% B_2O_3
7	$BaTi_{1.02}O_3$ + 0.25 mol% Sb_2O_3 + 2.0 mol% B_2O_3
8	$BaTi_{1.02}O_3$ + 0.25 mol% Sb_2O_3 + 2.0 mol% SiO_2

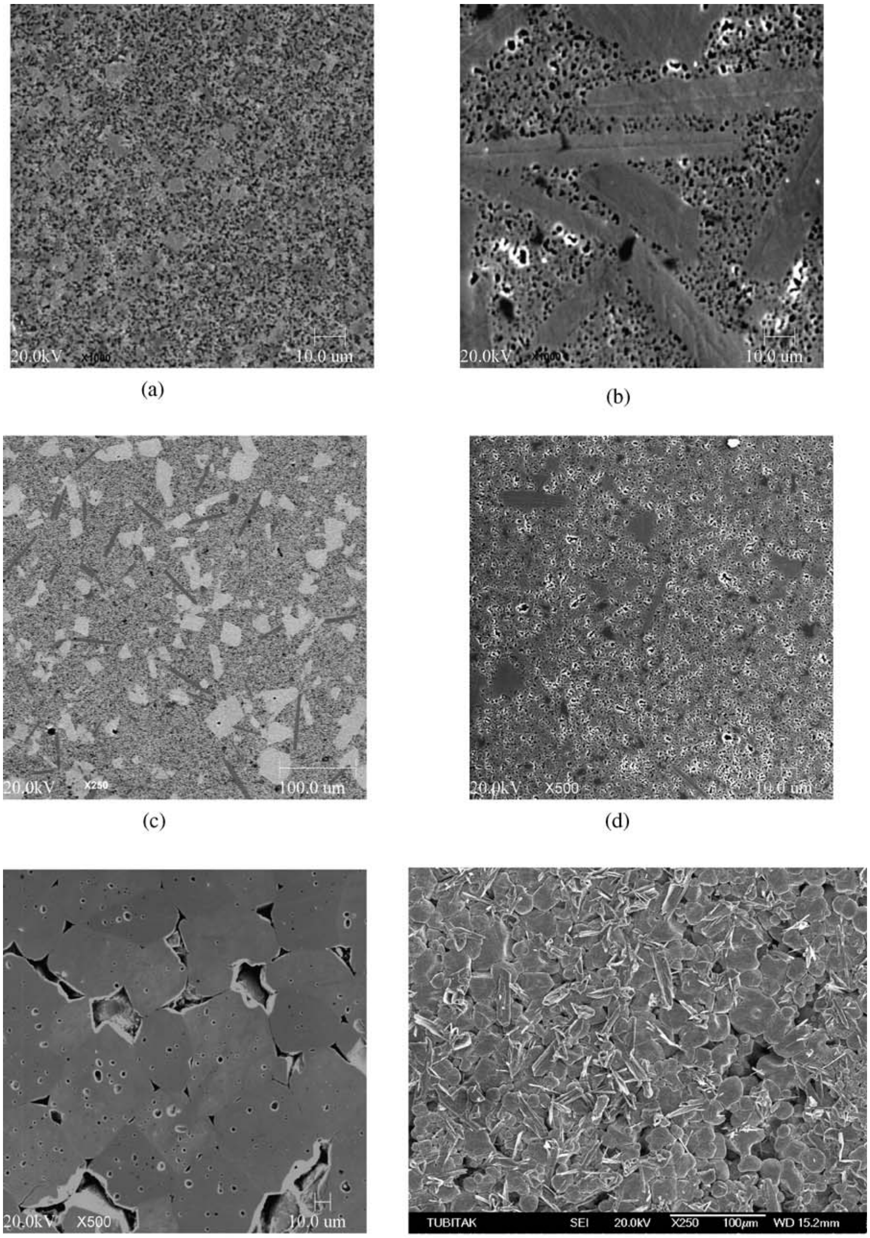
3. Results and discussion

The microstructures of the stoichiometric and non-stoichiometric $BaTiO_3$ (BT) samples (codes 1, 2, 21 and 3) sintered at 1300 °C for 1 h are shown in Fig. 1. The backscattered image of the Ba and Ti-excess samples in Fig. 1a, e are given in Fig. 1b, f. The bright polygonal grains indicate a Ba-rich phase and the dark platelet type structure indicates a Ti-rich phase. This Ti-rich phase consists of microcrystalline grains aligned linearly, forming the platelet type structure, which is clearly seen in the backscattered image. The XRD studies for the samples with Ba excess, stoichiometric and Ti-excess compositions sintered at 1250 °C for 1 h were given in Ref.[4] The secondary phase peaks fit the diffraction patterns of $Ba_4Ti_{12}O_{27}$ (PDF No: 44-0013) or $Ba_2Ti_5O_{12}$ (PDF No: 17-0661) which show similar diffraction peaks at Bragg angles very close to each other but differ only in intensities. Hence, the platelet type dark phase in Fig. 1b and f must be Ti-rich phase. The stoichiometric sample sintered at 1250 °C for 1 h exhibited small-grained porous structure. When the sintering temperature was increased to 1300 °C polygonal grains developed of the order of 25–30 µm in size within the fine-grained structure (Fig. 1c). The samples prepared with $TiCl_3$ showed a similar structure when sintered at 1250 °C. However, when the sintering temperature was increased to 1300 °C rapid growth occurred with a large amount of pores trapped within the grains (Fig. 1d). The densification rate of the sample coded 1, 2, 3 and 21 at different sintering temperatures are shown at Ref.[4] This showed that the $TiCl_3$ addition enhanced the densification.



(a) (b)

Fig. 2. Microstructures of $BaTiO_3$ sintered for 1 h at: (a) 1250 °C (code 7), (b) 1300 °C (code 7).



(a) (b) (c) (d) (e) (f)

Fig. 3. Microstructures of $BaTiO_3$ sintered for 10 h: (a) Ti-excess (code 3), 1250 °C, (b)Ti-excess + Sb_2O_3 (code 4), 1250 °C, (c)Ti-excess + Sb_2O_3 + 0.5 mol% B_2O_3 (code 5), 1250 °C, (d) code 5 prepared with $TiCl_3$ (code 51), 1250 °C, (e) Ti-excess + Sb_2O_3 + 2.0 mol% B_2O_3 (code 7), 1250 °C, (f) Ti-excess + Sb_2O_3 + 2.0 mol% B_2O_3 (code 7), 1300 °C.

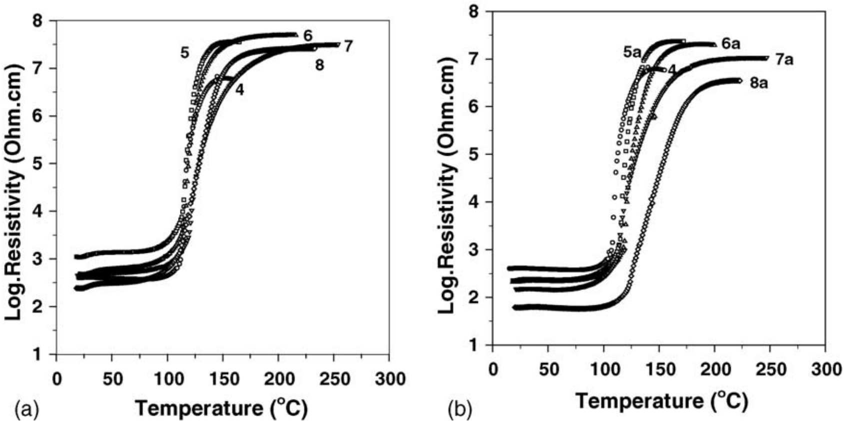


Fig. 4. PTCR characteristics of the samples: (a) Sintering aid added before calcination (1300 °C/1 h). (b) Sintering aid added after calcination (1300 °C/1 h).

The microstructure of the samples sintered at 1200 and 1250 °C for 1 h revealed a fine-grained matrix.[5] The addition of 0.5 mol% B_2O_3 caused bimodal, non-uniform, exaggerated grain growth in a fine-grained matrix. When the B_2O_3 content was raised to 1 mol% the number of abnormally grown grains increased. The 2 mol% B_2O_3 addition resulted in sudden grain growth with large pores trapped among the grains. The fine-grained matrix attached to the surfaces of the large grains within the pore cavities can be clearly seen in Fig. 2a. This indicates a solution and precipitation mechanism during liquid phase sintering. When the samples were sintered at 1300 °C, this mechanism gave rise to very large grain growth with a layered-structure on the grain surfaces as shown in Fig. 2b

The XRD results of the B_2O_3-added samples, which were given in Ref.[5] do not show any phases related to B_2O_3, which indicates either the loss of B_2O_3 by evaporation from the structure or to its presence as an amorphous phase. The densification curves,[5] showed that, the B_2O_3 addition also enhanced densification and brought the maximum densification to below the 1250 °C.

When the sintering time was increased to 10 h at 1250 °C, the undoped Ti-excess sample (code 3) exhibited polygonal grains ~3–5 μm in size in a very fine-grained matrix (Fig. 3a). The Sb_2O_3-added Ti-excess composition (code 4) showed very long elongated plate-like grains containing twin lamellae within a porous matrix of fine grains as shown in Fig. 3b. Twin formation in the composition coded 4 can be attributed to the solid state reaction by the diffusion of Sb^{5+} ions to Ti lattice sites giving rise to Ti^{3+} ions due to the charge compensation mechanism which can be represented by the formulae $Ba(Ti^{4+}{}_{1\text{-}0.01}\,Ti^{3+}{}_{0.005}\,Sb^{5+}{}_{0.005})O_3$. The microstructure of the 0.5 mol% B_2O_3 added to Sb_2O_3-doped Ti-excess sample (coded 5) shown in Fig. 3c revealed a different structure to that of the Sb_2O_3-added Ti-excess sample. In the former sample the microstructure showed polygonal grains containing twin lamellae and Ti-rich rod-like grains dispersed in a fine-grained matrix. The possible source for this rod-like Ti-rich phase is chemical inhomogeneities arising during the processing of the samples. In order to elucidate the mechanism, a sample was prepared by the same method but 0.2 mol% excess TiO_2 was added in a liquid $TiCl_3$ form. The size and the number of the twin-containing polygonal grains also decreased when the excess Ti was added in a liquid $TiCl_3$ form. The increased level of liquid phase in the 2 mol% B_2O_3 addition sample (coded 7) resulted in sudden uniform grain growth with pores trapped among the grains when sintered at 1250 °C for 10 h (Fig. 3e). The result indicates that 2 mol% B_2O_3 doping suppressed the twin formation.

The microstructure of all compositions sintered at 1300 °C for 1 h were given in Ref.[7], in order to compare the effect of the sintering aids added before and after the calcination step. The addition of sintering aids after the calcination step in the processing of BT improved the uniformity of the grains and affected the distribution of the pores within the microstructure. The additions of H_3BO_3 after the calcination step in the processing of BT samples also resulted in the formation of needle-like secondary phases within the structure (Fig. 3f).

The electrical properties of all the compositions sintered at 1200, 1250 and 1300 °C for 1 h were investigated. The samples sintered at 1200 °C exhibited insulating behaviour indicating that the SiO_2 and H_3BO_3 addition used to promote the liquid phase sintering were inadequate for the grain growth at this sintering temperature. When the sintering temperature was increased to 1300 °C all compositions become semiconducting, independent of their processing conditions (Fig. 4). The addition of the grain-boundary modifiers after the calcination step is more effective in sweeping out the impurities from the grain boundaries by combining them with a secondary phase. In all B_2O_3-containing samples the PTCR curves became steeper with the reduced amount of B_2O_3. The samples containing SiO_2 added before and after the calcination step (codes 8, 8a) gave a broader PTCR step than the 0.5 and 1.0 mol% B_2O_3-added samples. The broadening observed in the PTCR characteristics with the increased boron content can therefore be explained by the increased amount of the boron-containing secondary phase as depicted in the microstructure (Fig. 3f).

4. Conclusions

The Ti-excess samples contain the Ti-rich platelet $Ba_2Ti_5O_{12}$ phase. This phase and platelet-type structures are suppressed by increasing the B_2O_3 content and the sintering temperature. The addition of B_2O_3 to barium titanate promotes sintering at low temperatures by the formation of a liquid phase.

The Sb_2O_3-added Ti-excess composition revealed long elongated plate-like grains containing twin lamellae within a porous matrix of fine grains. The Sb_2O_3 donor doping at the 0.25 mol% level was very effective for promoting the twin formation due to the increased concentration of the Ti^{3+} ions. The 0.5 mol% B_2O_3 addition to the Sb_2O_3 donor-doped Ti-excess composition modified grain morphology from long elongated plates to polygonal type grains.

At the 2 mol% B_2O_3 addition level sudden grain growth occurred with the loss of twin lamellae from the structure. The addition of 0.2 mol% excess TiO_2 in liquid $TiCl_3$ form to the 0.5 mol% B_2O_3 containing Sb_2O_3 donor-doped BT sample reduced the size and the number of polygonal grains which contained twins. The addition of excess TiO_2 in liquid $TiCl_3$ form had a marked effect on the twin formation due to the homogeneous distribution of the excess Ti ions.

The addition of modifiers before the calcination step resulted in coarse porosity between the grains whilst the additions after calcination gave rounded, uniform grains with a pronounced decrease in porosity.

The increment of the liquid phase due to the increased H_3BO_3 addition gave rise to the reduction in the grain size. The addition of H_3BO_3 after the calcination step in the processing of the BT samples also resulted in the formation of needle-like secondary phases within the structure. The 0.5 mol% B_2O_3 added before calcination gave rise to insulating behaviour when sintered at 1250 °C for 1 h, but led to conducting characteristics when the boron was added after the calcination step.

The Sb_2O_3 donor-doped BT showed a PTCR effect of 4.2 orders of magnitude and the B_2O_3 and SiO_2-added samples showed PTCR effects of 4.5–5.0 orders of magnitude. In all the B_2O_3-contained samples the PTCR curves became steeper with a reduced amount of B_2O_3.

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