SEMI-CONDUCTING BARIUM TITANATE CONTAINING B$_2$O$_3$

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The effects of the grain boundary modifiers H$_3$BO$_3$ and SiO$_2$ before and after the calcination steps on the microstructure and on the positive temperature coefficient of resistivity (PTCR) of Sb$_2$O$_3$ donor-doped Ti-excess barium titanate (BT) were investigated. The additions before calcination resulted in coarse porosity between the grains and the additions after calcination gave rounded, uniform grains with a pronounced decrease in porosity. The Sb$_2$O$_3$ donor-doped BT became conductive when sintered at 1300°C giving a room temperature resistivity (ρ_{RT}) of 400 Ohm cm. The ρ_{RT} values of the B$_2$O$_3$ and SiO$_2$ contained samples decreased when modifiers were added after the calcination step. The Sb$_2$O$_3$ donor-doped BT showed a PTCR effect of 4.2 orders of magnitude and a range of 4.5-5.0 orders of magnitude were obtained for the B$_2$O$_3$ and SiO$_2$ added samples.

INTRODUCTION

The pure BaTiO$_3$ (BT) ceramic insulator having a perovskite structure becomes semiconducting after doping with the trivalent donors (La, Sb, Y) which are substituted for the Ba^{+2} or with pentavalent donors (Sb, Nb, Ta) which are substituted for the Ti^{+4} [1,2]. The insulating BT is transformed into an n-type semiconducting perovskite and the resistivity increases by several orders of magnitude when heated above the Curie temperature (T_C) where the material goes through a ferroelectric to paraelectric phase transformation [2,3]. This behaviour is known as the Positive Temperature Coefficient of Resistance (PTCR) effect. The magnitude of the PTCR effect depends on many factors; donor and acceptor-dopant concentration, grain-size, sintering temperature and time, oxygen partial pressure, the stochiometry of the BT compositions (Ba/Ti ratio) and to the liquid phase added as a sintering aid. Hence, the optimisation of the microstructure by the control of the process parameters to improve the electrical properties is a prime concern. BT ceramics are sintered at temperatures between 1300-1350°C. Therefore a great deal of research has been carried out to improve the grain growth by liquid phase sintering either by altering the cation stochiometry or by adding some liquid-forming sintering aids. Many oxides such as Bi$_2$O$_3$, LiF, B$_2$O$_3$, SiO$_2$ and Al$_2$O$_3$ [4-8] have been used for the formation of the required liquid phase to enhance densification and grain growth in the BT based ceramics. Various suggestions were put forward by several researchers for explaining the PTCR in BT. All of them agree that it is closely related to the microstructure of the samples. According to Ho [7] there is a tendency that the room temperature resistivity decreases while the mean grain size increases with sintering temperatures. Also Fa Lin and Ti Hu [9] reported high electrical resistivity and poor PTCR behaviour which is generally observed for the fine grain materials. In other words, low room temperature resistivity and good PTCR characteristics are found for the large grain (> 10 µm) materials. They also reported that a good PTCR property is obtained for even fine grain and high density materials, provided that the appropriate cooling procedure is applied. However, Kuwabara [10] reported that a material of 2-5 m grain size possesses good PTCR behaviour as long as it had a high porosity.

The conduction mechanisms of the PTCR behaviour of semiconducting BT were proposed by Heywang [11] and Jonker [12] in which the high resistivity was ascribed to the formation of Schottky barriers at the grain boundaries and the low value of room temperature resisitvity is presumed to be caused by the charge compensation due to the spontaneous polarization. Zajc [13] observed that the resistivity of the samples decreased when the sintering temperature was increased.

Boron (B) containing compounds were also investigated as a liquid phase sintering of BT due to the low melting point of (460°C) [8]. Ho [7] reported that the incorporation of B into the peroskite structure is negligible and the presence of B at a grain boundary to promote the grain boundary acceptor type surface state, results in an enhancement of the PTCR effect. Jianquan [14] also reported that the PTCR effect of the BT ceram-

ics is enhanced distinctly, the room temperature resistivity (RT) is increased by doping with B_2O_3 vapour. He proposed that the interstitial boron and/or the complex of neutral barium vacancies are responsible for the enhancement of the PTCR effect.

Hence, this work was carried out in order to study the effect of the boron addition in the form of H_3BO_3 to the microstructure and to the PTCR characteristics of the Ti-rich (Ba/Ti = 0.98) $BaTiO_3$ ceramics containing 0.25 mol% Sb_2O_3 used as a semi-conductive additive. 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.

EXPERIMENTAL

The barium titanate (BT) compositions were prepared by the conventional ceramics processing techniques. The compositions prepared are given below.

Code: Compositions:
1   $BaTi_{1.02}O_3$ + 0.25 mol% Sb_2O_3
2   $BaTi_{1.02}O_3$ + 0.25 mol% Sb_2O_3 + 2.0 mol% SiO_2
3   $BaTi_{1.02}O_3$ + 0.25 mol% Sb_2O_3 + 0.5 mol% B_2O_3
4   $BaTi_{1.02}O_3$ + 0.25 mol% Sb_2O_3 + 1.0 mol% B_2O_3
5 $BaTi_{1.02}O_3$ + 0.25 mol% Sb_2O_3 + 2.0 mol% B_2O_3

The $BaCO_3$ (BDH-272885Y), TiO_2 (Fisher-780915) and Sb_2O_3 (Merck-7836) and H_3BO_3 were weighed according to the mol formula of the compositions and milled in an ashless rubber-lined jar for 5 hours using ZrO_2 balls and deionised water as a grinding media. The ground mixture was then dried at 110°C. During the drying process, the mixture was stirred frequently in order to mix the water-soluble H_3BO_3 homogeneously. Cakes were prepared from the mixture in a steel die of 50 mm diameter at 15 MPa without using any binder. The calcinations of the cakes were carried out at 1000°C for 2 hours employing a 200°C/h heating rate. The calcined material was then crushed to < 0.5 mm and reground for 5 hours in the stated conditions. The median diameter of the ground powder was found to be 1.2 μm. After drying the ground material granulation was done using distilled water as a binder. Granules were die-pressed into discs of 17 mm in diameter and 4 mm in thickness under a pressure of 100 MPa. The samples were sintered in air at 1200, 1250 and 1300°C for 1 hour employing a 300°C/h heating rate and then cooled naturally in the furnace. The sintered samples were electroded with flame-sprayed aluminium to provide ohmic contact. This processing method was

employed in all compositions coded 1-5. The sub-codings a and b were used in the composition 2-5 which denote the addition of sintering aids H_3BO_3 and SiO_2 before and after the calcination steps, respectively.

The microstructure of the samples was studied using a scanning electron microscope (Jeol JSM 5600). The phases were identified by X-ray diffraction (XRD-6000 Shimadzu-Japan) using CuKα radiation at 40 kV/30 mA. The temperature dependence of resistance was measured with 9 V multimetre in a temperature programmable furnace at a heating rate of 3°C/min. from 20-300 C using a jig having spring-pushed Cu rods of 8 mm diameter.

RESULTS AND DISCUSSION

The microstructure of all compositions sintered at 1300°C for 1 hour are given in figure 1 in order to compare the effect of the sintering aids added before and after the calcination step. The Sb_2O_3 donor-doped Ti rich composition coded 1 showed porous microstructure with a grain size of 10-20 μm (figure 1a). The SiO_2 addition to this composition before the calcination step increased the mean grain size to 30 μm and resulted in coarse porosity between the grains (figure 1b). The addition of SiO_2 after the calcination step gave rise to uniform grains of 20-25 μm in size and reduced the pore coarsening between the grains (figure 1c). However, when 0.5 mol% H_3BO_3 was used as a grain boundary modifying sintering aid instead of SiO_2 before the calcination step resulted in uniform large grains of 40-50 μm in size (figure 1d). The addition of H_3BO_3 also resulted in coarse porosity between the grains as observed in the SiO_2 added sample 2a, but the pores were more uniformly distributed within the structure. However, the addition of 0.5 mol% H_3BO_3 after calcination gave rounded and uniform grains of 30 μm of mean size with a pronounced decrease in porosity (figure 1e) when compared to the H_3BO_3 addition before the calcination (figure 1d). The sample 3b also had a larger grain structure and less porosity when compared to the SiO_2-added sample 2b after the calcination step. Hence, 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 addition of 1 mol% H_3BO_3 before the calcination step revealed a similar microstructure to that of sample 3a, but the grain size increased to 50-70 μm (figure 1f). The addition of 1 mol% H_3BO_3 after the calcination step also showed a rounded grain structure (figure 1g) as observed in the 0.5 mol% H_3BO_3 added sample 3b. The morphology obtained in these samples was also observed in the samples with a 2 mol% H_3BO_3 addition before and after the calcination step (figure
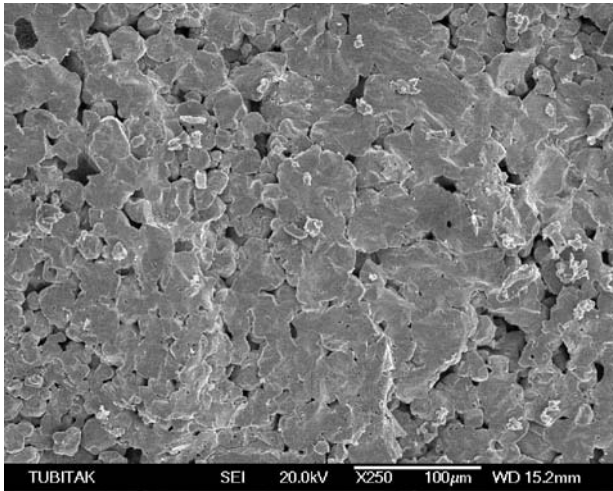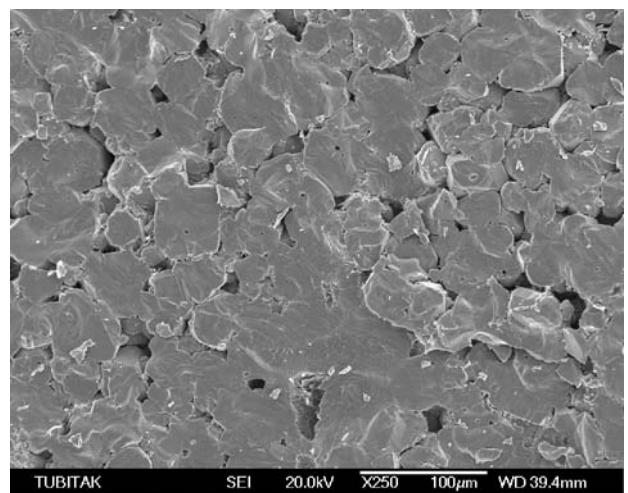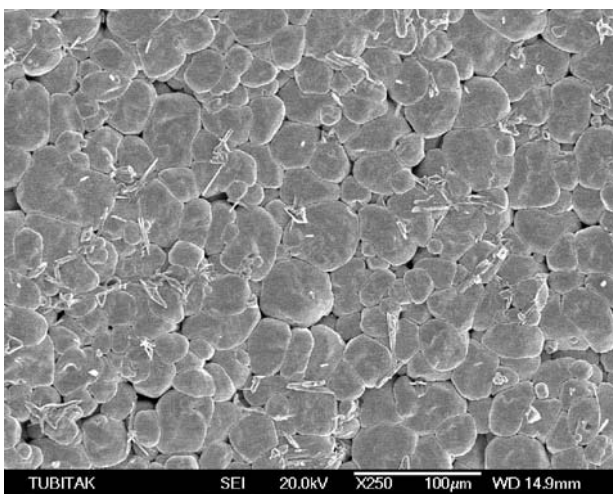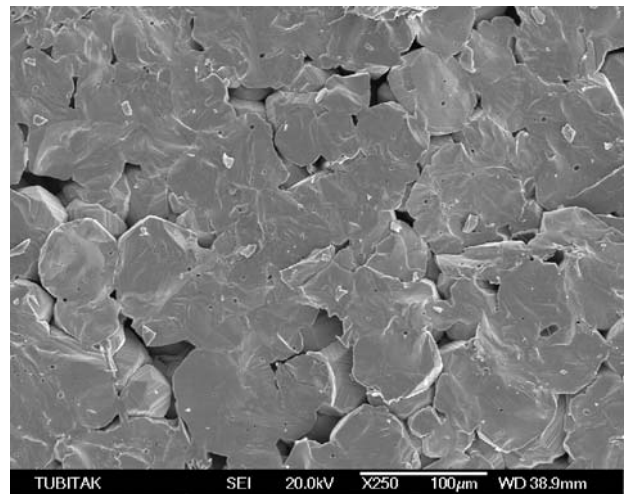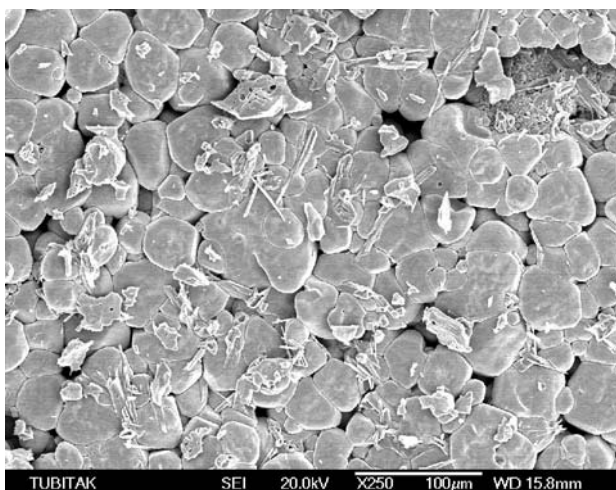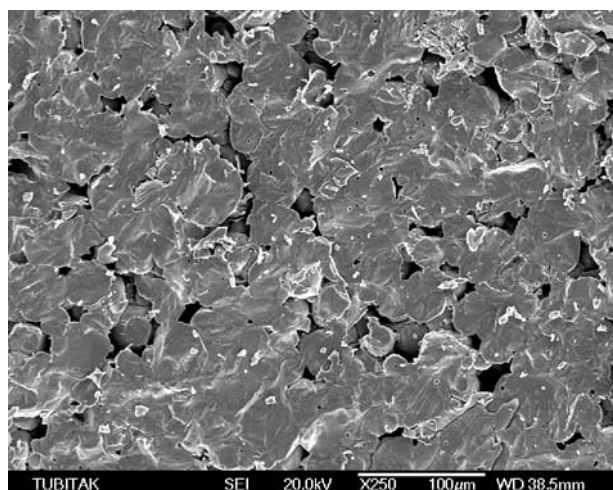
a)
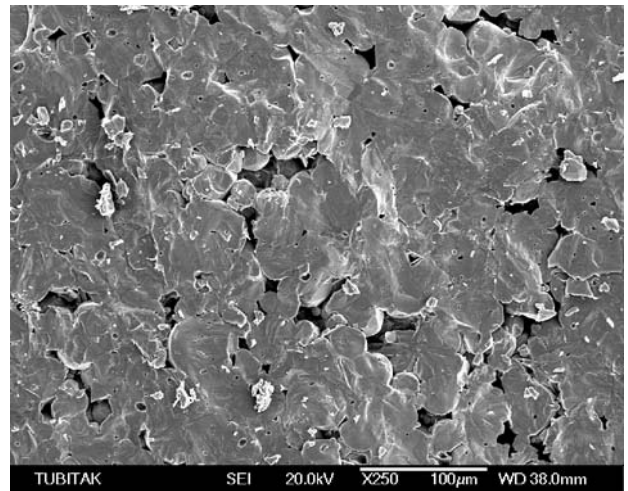
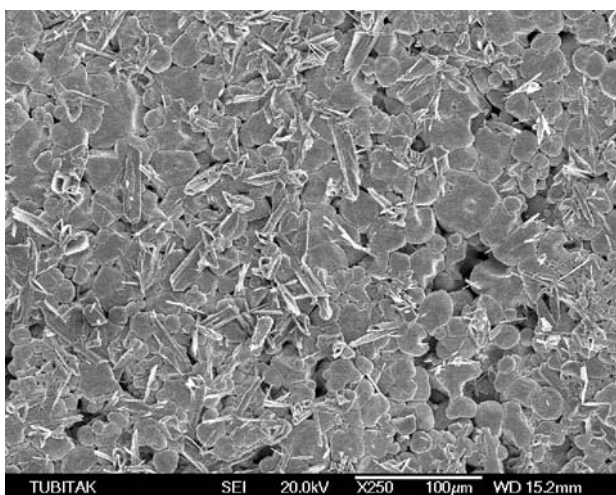

b)
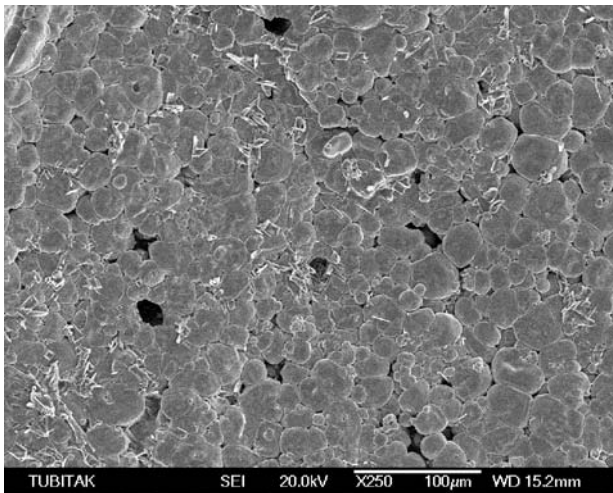
c)

d)

e)

f)

Figure 1. Micrographs of the samples sintered at 1300°C for 1 hour; (a) Composition 1, (b) Composition 2a, (c) Composition 2b, (d) Composition 3a, (e) Composition 3b, (f) Composition 4a.

g)

h)

i)

Figure 1. Micrographs of the samples sintered at 1300°C for 1 hour; (g) Composition 4b, (h) Composition 5a, (i) Composition 5b.

1h,i). The increment of the liquid phase due to the increased H_3BO_3 addition gave rise to the decrement in the grain size. The additions of H_3BO_3 after the calcination step in the processing of the BT sample also resulted in the formation of needle- like secondary phases within the structure. The microstructure studies carried out at higher magnifications revealed that this phase was either in a needle shape or in a fine plate-like form placed within the pores at the grains junctions. The amount of this phase increased with the increasing amount of the H_3BO_3 addition level (figure 1g,i).

The XRD patterns of samples containing 2 mol% H_3BO_3 and 2 mol% SiO_2 added before and after the calcination step coded as 2a, b and 5a, b, respectively and sintered at 1300°C for 1 hour are depicted in figure 2. The diffraction peaks were identified as the tetragonal BT phase and a small amount of cubic BT phase (PDF No: 050-626, PDF No: 31-0174) marked as *T* and *C* respectively on the patterns. The XRD patterns of boron-added samples did not show any diffraction

peaks related to the needle-like secondary phase observed in the microstructures shown in figure 1g and 1i. Therefore, this indicates the solidification of the boron-rich liquid phase in an amorphous form. Hari and Kutty [4] have also reported similar results in which the B_2O_3 additions resulted in the formation of a distinct secondary phase but could not be identified by XRD. They concluded that B_2O_3 formed a glassy phase having a composition of BaB_6TiO_{12}. Rhim et al [8] have also reported similar results in which they concluded that the B_2O_3 addition to BT formed a liquid phase at a low temperature which promoted the sintering and remained within the microstructure as a secondary phase. However, they did not confirm the nature of this secondary phase. The XRD patterns of the SiO_2 addition before and after the calcination steps also showed the tetragonal BT as a main phase and the presence of a small amount of cubic BT. These patterns showed two small peaks at Bragg Angels (2θ) between 27-28 degrees, which indicated the presence of a different phase possibly related with SiO_2. Although, it is difficult to identify this phase from the two diffraction peaks, a systematic investigation carried out on all PDF files related to the BT-SiO_2 system indicated by $Ba_2TiSi_2O_8$ phase (PDF No: 22-0513), in contrast to the phase $BaTiSi_3O_9$ reported by Hari and Kutty.

The electrical properties of all the compositions sintered at 1200, 1250 and 1300°C for 1 hour 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 temper-

ature. For the same reason, in sinterings at 1250°C, the sample coded 1, which contained no grain boundary liquid phase modifier and the sample coded 3a, which contained 0.5 mol% H_3BO_3 added before the calcination step also showed no semiconductive property. The resistivity of the donor-doped Sb_2O_3 (code 1) and the other compositions containing sintering aids added before and after the calcination step are given in figure 3a-d as a function of temperature. The samples containing SiO_2 and 1, 2 mol% B_2O_3 added before calcination showed semiconduction when sintered at 1250°C (figure 3a). Though 0.5 mol% B_2O_3 addition before calcination gave insulating property at this temperature became conductive when the boron addition was done after the calcination step (figure 3b). When the sintering temperature was increased to 1300°C all compositions become semiconductive independent to their processing conditions (figure 3c,d). All curves of ρ versus T in figure 3a-d showed nearly the same Curie temperature at which a sudden rise in resistivity began at about 120°C. The temperature at which resistivity reached it maximum (T_{max}) was found to have different values for different samples and ranged from 150-290°C as seen in figure 3a-d. The samples containing 2 mol% B_2O_3-added before calcination (coded 5a in figure 3a,c) showed higher T_{max} values of 290 and 250°C when sintered at 1250 and 1300°C respectively. The donor-doped Sb_2O_3 (code 1) which did not show semiconductivity when sintered at 1250°C became conductive when sintered at 1300°C giving a room temperature resistivity of 400 Ohm cm. The room temperature resistivity (ρ_{RT}) values of the B_2O_3-added samples increased when the modi-

fiers were added to this composition before the calcination step whereas, the SiO_2 addition decreased this ρ_{RT} value to 240 Ohm cm. However, when 0.5, 1.0 and 2.0 mol% B_2O_3 were added after the calcination step, the room temperature resistivity values dropped from 400 Ohm cm to the values of 225, 210 and 150 Ohm cm respectively and 63 Ohm-cm for the SiO_2-added sample. This shows the effectiveness of the processing conditions in the production of the BT. Kutty and Hari [15] also observed that the addition of Al_2O_3 before the calcination step resulted in a high RT but, addition after the calcination step gave rise to lower room temperature resistivity. This again indicates that the processing conditions strongly affect the microstructure and the electrical properties of BT. Hence, these results strongly support the view that the grain boundary modifiers used in this work wash out the impurities which give rise to the acceptor levels at the grain surfaces. Therefore the washout process reduces the Schotky barriers that affect the PTCR properties of BT. 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. Hence, the room temperature resistivity of BT can be lowered by the addition of the grain boundary modifier after the calcination step. The Sb_2O_3 donor-doped BT coded 1 showed a PTCR effect of about 4.2 orders of magnitude and the other compositions gave slightly higher values in the range of 4.5 -5.0 orders of magnitude. Ho [7] reported that the presence of boron at a grain boundary promoted the grain boundary surface state (or acceptor-type state) density and thus enhanced
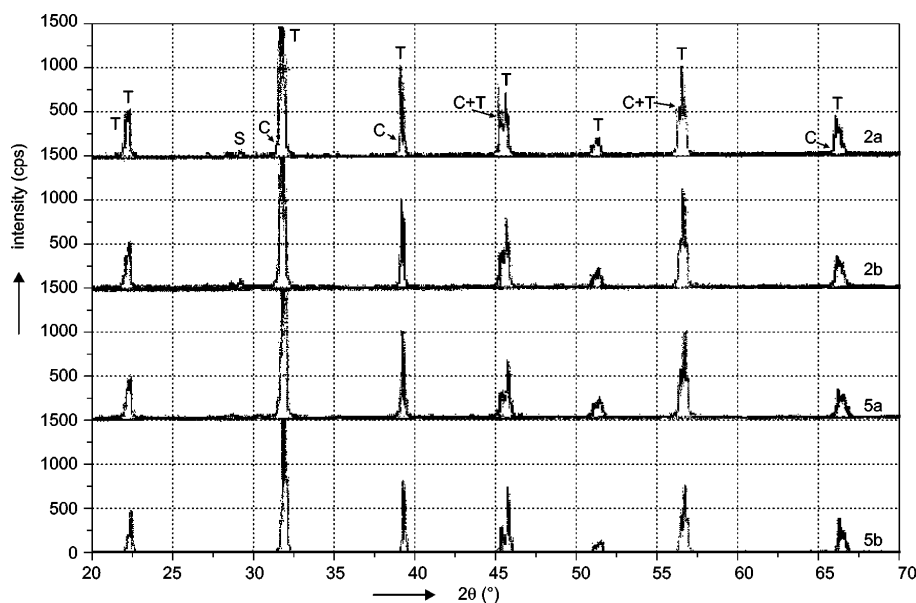
Figure 2. XRD patterns of $BaTiO_3$ sintered at 1300°C for 1 hour; (2a) 2.0 mol% SiO_2 added before calcinations, (2b) 2.0 mol% SiO_2 added after calcinations, (5a) 2.0 mol% B_2O_3 added before calcinations, (5b) 2.0 mol% B_2O_3 added after calcinations.

the PTCR effect. In all B$_2$O$_3$-containing samples the PTCR curves became steeper with the decreased amount of B$_2$O$_3$ content. The samples containing SiO$_2$ added before and after the calcination step (2a, 2b) gave a broader PTCR jump than the 0.5 and 1.0 mol% B$_2$O$_3$-added sample. According to Hari and Kutty [4] SiO$_2$ does not form any solid solutions with BaTiO$_3$. This broadening was the resulting of identifiable distinct silica-containing secondary phases, like BaTiSi$_3$O$_9$ along

grain boundaries or triple junctions of the grains. Hence, they pointed out that the broadening of the ρ-T characteristics indicate the enhanced disorder at the grain boundary layers by the formation of some secondary phases. The broadening observed in the PTCR characteristics with the increased boron content can therefore be explained with the increased amount of the boron-containing secondary phase as depicted in the microstructure given in the figure 1i.
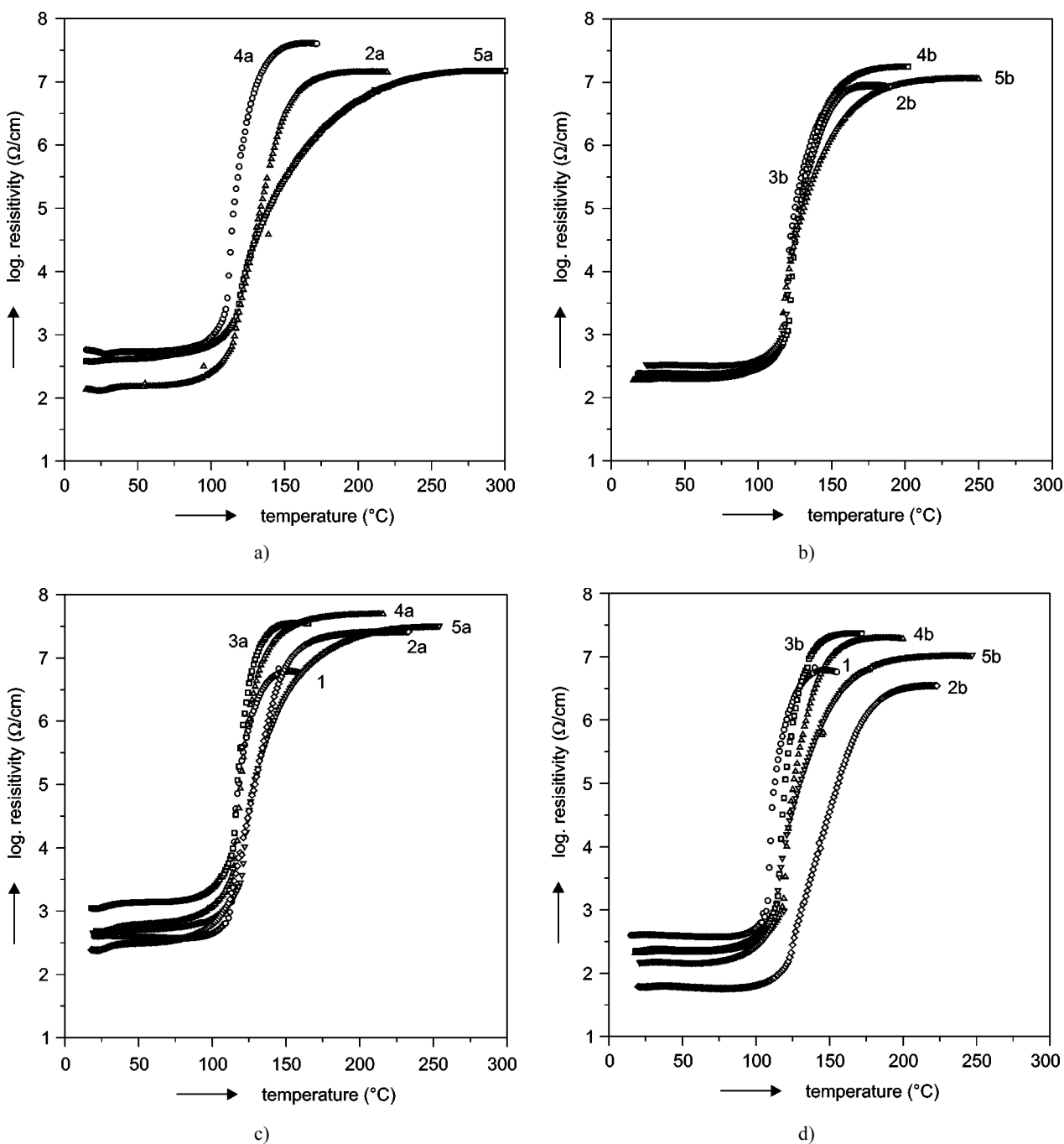

Figure 3. PTCR characteristics of the samples; (a) Sintering aids added before calcination (1250°C/ 1 hour), (b) Sintering aids added after calcination (1250°C/ 1 hour), (c) Sintering aids added before calcination (1300°C/ 1 hour), (d) Sintering aids added after calcination (1300°C/ 1 hour).

CONCLUSIONS

The addition of the grain boundary modifiers such as H_3BO_3 and SiO_2 before and after the calcination step in the processing of barium titanate revealed the following:

- The addition of modifiers before the calcination step resulted in coarse porosity between the grains and 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 decrement in the grain size. The addition of H_3BO_3 after the calcination step in the processing of the BT sample also resulted in the formation of needle-like secondary phases within the structure. The amount of this phase increased with the increased amount of H_3BO_3 addition.
- The XRD patterns of the boron-added samples did not show any diffraction peaks related to the needle-like secondary phase observed in the microstructures, due to the solidification of the boron rich liquid phase in the amorphous form.
- The 0.5 mol% B_2O_3 added before calcination gave an insulating property when sintered at 1250°C for 1 hour, but became conductive when the boron addition was done after the calcination step.
- The Sb_2O_3 donor-doped BT became conductive when sintered at 1300°C giving a room temperature resistivity of (ρ_{RT}) 400 Ohm cm. The ρ_{RT} values of the B_2O_3 and SiO_2 contained samples decreased when modifiers were added after the calcination step. The processing conditions strongly affects the microstructure and the electrical properties of BT. Hence, these results strongly support the view that the modifiers help to wash out the impurities which give rise to acceptor levels at the grain surface. Therefore this wash-out process reduces the Schotky barriers which affect the PTCR properties of BT. Therefore 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 to a secondary phase. Hence, the room temperature resistivity of BT can be lowered by the addition of a grain boundary modifier 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 in the range of 4.5- 5.0 orders of magnitude. In all the B_2O_3-contained samples the PTCR curves became steeper with a decreased amount of B_2O_3 content. The broadening observed in the PTCR characteristics with the increased boron content can be explained by the increased amount of boron- contained secondary phase as depicted in the microstructure.

Acknowledgement

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POLOVODIVÝ TITANIČITAN BARNATÝ OBSAHUJÍCÍ B_2O_3

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Byl zkoumán vliv modifikátorů rozhraní H_3BO_3 a SiO_2 před a po žíhání na kladný teplotní koeficient odporu (PTCR) titaničitanu barnatého (BT) dopovaného Sb_2O_3 donorem a se stechiometrickým přebytkem Ti. Přídavky před žíháním vedly k hrubější po-rozitě mezi zrny a přídavky po žíhání vedly ke kulatým stejno-rodým částicím s výrazně zmenšenou porozitou. BT dopované Sb_2O_3 donorem se stávaly vodivými po sintrování při 1300°C s výslednou vodivostí 400 Ω cm při pokojové teplotě (ρ_{RT}). Hodnoty ρ_{RT} vzorků obsahujících B_2O_3 a SiO_2 klesaly, pokud modifikátory byly přidávány po kalcinaci. BT dopované Sb_2O_3 donorem měly PTCR 4.2 řády a vzorky s B_2O_3 a SiO_2 4.5 až 5 řádů.