INTRODUCTION

The pure BaTiO₃ (BT) ceramic insulator having a perovskite structure becomes semiconducting after doping with the trivalent donors (La, Sb, Y) which are substituted for the Ba²⁺ or with pentavalent donors (Sb, Nb, Ta) which are substituted for the Ti⁴⁺ [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 stoichiometry 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 stoichiometry or by adding some liquid-forming sintering aids. Many oxides such as Bi₂O₃, LiF, B₂O₃, SiO₂ and Al₂O₃ [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 resistivity 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 aid. The effects of the grain boundary modifiers H₃BO₃ and SiO₂ before and after the calcination steps on the microstructure and on the positive temperature coefficient of resistivity (PTCR) of Sb₂O₃ 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 Sb₂O₃ donor-doped BT became conductive when sintered at 1300°C giving a room temperature resistivity (ρ₉₅) of 400 Ohm cm. The ρ₉₅ values of the B₂O₃ and SiO₂ contained samples decreased when modifiers were added after the calcination step. The Sb₂O₃ 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 B₂O₃ and SiO₂ added samples.
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 electrodeed 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 multimeter 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 SiO_2 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_2BO_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
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.
The increment of the liquid phase due to the increased $\text{H}_3\text{BO}_3$ addition gave rise to the decrement in the grain size. The additions of $\text{H}_3\text{BO}_3$ 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 $\text{H}_3\text{BO}_3$ addition level (figure 1g,i).

The XRD patterns of samples containing 2 mol% $\text{H}_3\text{BO}_3$ and 2 mol% $\text{SiO}_2$ 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 $\text{B}_2\text{O}_3$ additions resulted in the formation of a distinct secondary phase but could not be identified by XRD. They concluded that $\text{B}_2\text{O}_3$ formed a glassy phase having a composition of $\text{BaB}_6\text{TiO}_{12}$. Rhim et al [8] have also reported similar results in which they concluded that the $\text{B}_2\text{O}_3$ 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 $\text{SiO}_2$ 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 (2$\theta$) between 27-28 degrees, which indicated the presence of a different phase possibly related with $\text{SiO}_2$. 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-$\text{SiO}_2$ system indicated by $\text{Ba}_2\text{TiSi}_2\text{O}_8$ phase (PDF No: 22-0513), in contrast to the phase $\text{BaTiSi}_3\text{O}_9$ 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 $\text{SiO}_2$ and $\text{H}_3\text{BO}_3$ 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% H₃BO₃ added before the calcination step also showed no semiconductive property. The resistivity of the donor-doped Sb₂O₃ (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 SiO₂ and 1, 2 mol% B₂O₃ added before calcination showed semiconduction when sintered at 1250°C (figure 3a).

Though 0.5 mol% B₂O₃ 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 became 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% B₂O₃-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 Sb₂O₃ (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 B₂O₃-added samples increased when the modifiers were added to this composition before the calcination step whereas, the SiO₂ addition decreased this ρ_RT value to 240 Ohm cm. However, when 0.5, 1.0 and 2.0 mol% B₂O₃ 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 SiO₂-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 Al₂O₃ 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 Schottky 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 Sb₂O₃ 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
the PTCR effect. In all B₂O₃-containing samples the PTCR curves became steeper with the decreased amount of B₂O₃ content. The samples containing SiO₂ added before and after the calcination step (2a, 2b) gave a broader PTCR jump than the 0.5 and 1.0 mol% B₂O₃-added sample. According to Hari and Kutty [4] SiO₂ does not form any solid solutions with BaTiO₃. This broadening was the resulting of identifiable distinct silica-containing secondary phases, like BaTiSi₃O₉ 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 H3BO3 and SiO2 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 H3BO3 addition gave rise to the decrement in the grain size. The addition of H3BO3 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 H3BO3 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% B2O3 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 Sb2O3 donor-doped BT became conductive when sintered at 1300°C giving a room temperature resistivity of (ρRT) 400 Ohm cm. The ρRT values of the B2O3 and SiO2 contained samples decreased when modifiers were added after the calcination step. The processing conditions strongly affect 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 Schottky 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 Sb2O3 donor-doped BT showed a PTCR effect of 4.2 orders of magnitude and the B2O3 and SiO2-added samples showed in the range of 4.5-5.0 orders of magnitude. In all the B2O3- and SiO2-contained samples the PTCR curves became steeper with a decreased amount of B2O3 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.

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References


POLOVODIVÝ TITANIČITAN BARNATÝ OBSAHUJÍCÍ B2O3

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Byl zkoumán vliv modifikátorů rozhraní H3BO3 a SiO2 před a po žháraní na kladný teplotní koeficient odporu (PTCR) titaničitanu barnatého (BT) dopovaného Sb2O3 donorem a se stechiometrickým přebytělem Ti. Přídavky před žháním vedly k tvorbě po rozdělění mezí zrny a přídavky po žháraní vedly ke kulatým stejno-rodým částicím s výrazně zmenšenou porozitou. BT dopované Sb2O3 donorem se stávaly vodivými při 1300°C s výslednou vodivostí 400 Ohm cm při pokojové teplotě (ρRT). Hodnoty ρRT vzorků obsahujících B2O3 a SiO2 kle- saly, pokud modifikátoru byly přidávány po kalcinaci. BT dopované Sb2O3 donorem měly PTCR 4.2 řády a vzorky s B2O3 a SiO2 4.5 až 5 řádů.