ORIGINAL ARTICLE

Effects of surrounding powder in sintering process on the properties of Sb and Mn- doped barium-strontium titanate PTCR ceramics

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Abstract

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In this research, the effects of surrounding powder used during sintering of Sb and Mn doped barium-strontium titanate (BST) ceramics were studied. The ceramic samples were prepared by a conventional mixed-oxide method and placed on different powders during sintering. Phase formation, microstructure and PTCR behavior of the samples were then observed. Microstructures and PTCR behavior varied with the type of surrounding powder, whereas the crystal structure did not change. The surrounding powder has more effects on the shape of the grain than on the size. The grain size of samples was in the range of 5-20 µm. The most uniform grain size and the highest increase of the ratio of ρ_{max}/ρ_{RT} were found to be about 10^6 for samples which had been sintered on Sb-doped BST powder. This value was an order of magnitude greater than for samples sintered on a powder of the equivalent composition to that of the sample pellet.

Key words : barium- strontium titanate, microstructure, PTCR, sintering process

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บทคัดย่อ

พรสุดา บ่มไล่

อิทธิพลของผงรองพื้นที่ใช้ในขั้นตอนการซินเตอร์ต่อสมบัติต่าง ๆ ของเซรามิกแบเรียม-สทรอนเชียมไทเทเนตที่มีสัมประสิทธิ์อุณหภูมิเชิงบวกเมื่อเจือด้วยแอนติโมนีออกไซด์และแมงกานีสออกไซด์

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ในการวิจัยนี้ได้ทำการศึกษาอิทธิพลของผงรองพื้นที่ใช้ในขั้นตอนการซินเตอร์ของเซรามิกแบเรียม-สทรอนเชียมไทเทเนต สารตัวอย่างเตรียมขึ้นโดยวิธีผสมออกไซด์แบบดั้งเดิมและวางบนผงต่างชนิดกันในขั้นตอนการซินเตอร์ จากนั้นได้ทำการตรวจสอบพฤติกรรมการเกิดเฟส โครงสร้างจุลภาคและสมบัติทางไฟฟ้าของสารตัวอย่าง ผลการทดลองพบว่าโครงสร้างจุลภาคและสมบัติพีทีซีอาร์มีค่าขึ้นอยู่กับชนิดของผงที่ใช้ในขั้นตอนการซินเตอร์ ในขณะที่โครงสร้างผลึกของสารตัวอย่างไม่เปลี่ยนแปลง ผงรองพื้นที่ใช้มีอิทธิพลต่อรูปร่างของเกรนมากกว่าขนาดเกรน โดยขนาดเกรนมีค่าประมาณ 5-20 ไมครอน สารตัวอย่างที่วางบนผงแบเรียม-สทรอนเชียมไทเทเนตที่เจือด้วยแอนติโมนีออกไซด์ มีขนาดเกรนที่ความสม่ำเสมอและอัตราส่วนของสภาพต้านทานไฟฟ้าสูงสุดต่อสภาพต้านทานไฟฟ้าที่อุณหภูมิห้องเพิ่มขึ้นสูงสุดประมาณ 6 ระดับขนาด ซึ่งค่านี้จะสูงกว่าในเซรามิกสารตัวอย่างที่วางบนผงที่มีองค์ประกอบเดียวกันกับในสารตัวอย่างประมาณ 1 ระดับขนาด

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It is well known that donor-doped barium titanate ($BaTiO_3$)-based ceramic exhibits positive temperature coefficient of resistivity (PTCR) behavior, and is widely used in over-current protection devices, self-regulating heaters, and temperature sensors in electronic circuits (He *et al*., 2002). This behavior was discovered in 1955 and refers to an abnormal increase of resistivity around the Curie temperature (T_C) (Goodman, 1963; Urek and Drofenik, 1999). The T_C can be shifted to lower temperatures by adding $SrTiO_3$ forming a solid solution of barium-strontium titanate (Zhao *et al*., 2001).

The most accepted conduction models explaining the sudden change of resistivity have been proposed by Heywang and Jonker; a potential barrier arises from the electron-trapping effect of surface acceptor states at grain boundary regions leading to high resistivity in the materials immediately above T_C (Haywang, 1964; Jonker, 1964). The lower resistivity of the materials at temperatures below T_C, results from the compensation of surface states due to spontaneous polarization which occurs within ferroelectric domains.

Low resistivity at room temperature and a strong PTCR effect are both critical parameters for device applications. It is reported that the PTCR characteristics of $BaTiO_3$-based ceramics are very sensitive to both the microstructure and the defect chemistry of the materials, which are strongly influenced by processing parameters such as chemical composition, and sintering conditions (Lin *et al*., 1990; Ihring, 1981; Basu *et al*., 1987). For example, the PTCR effect can be improved significantly by the presence of the acceptor dopants at the grain boundary (Ihring, 1981). In particular, the resistance jump can be enhanced considerably when ceramics are doped with 3d-elements, such as Mn, Fe and Cu, due to these elements acting as acceptors and increasing the surface state acceptor density (Basu *et al*., 1987).

Recently, a new process for introducing a donor dopant, the so-called vapour-doping method, involving doping with a vapour of a dopant oxide e.g. Bi_2O_3 vapour doping during sintering has been demonstrated to lead to a significant improvement in the PTCR effects (Qi *et al*., 1998; Chatterjee and Maiti, 2001; Qi *et al*., 2002; Qi *et al*., 2001). Therefore, it is important to consider the possible effect of any volatile oxides contained in the powders on which pellets are normally placed during sintering. The objective of this study is to investigate the effects of three different powder compositions on electrical properties and microstructure of Sb, Mn-modified BST ceramics. One powder was alumina, one BST containing Sb_2O_3 and MnO_2 (similar in composition to the doped BST pellet) and the other BST powder modified with Sb_2O_3 only.

Materials and Methods

Samples in this work were prepared by using the conventional mixing oxide process. Starting materials were $BaCO_3$, $SrCO_3$, TiO_2, Sb_2O_3, SiO_2 and MnO_2 (Aldrich Chemical Company, Inc., 99.9 + % purity) which were mixed in a ratio to produce the composition $[(Ba_{0.8}Sr_{0.2})TiO_3 + 0.15$ mol% $Sb_2O_3 + 1.0$ mol% $TiO_2 + 3.0$ mol% $SiO_2 + 0.005$ mol% $MnO_2]$. After ball-milling with zirconia grinding media and ethanol in a polypropylene jar for 24 hours, the mixture was dried, ground and then calcined in air at 1100ºC for 2 hours. The calcined powder was blended with 3 wt % polyvinyl alcohol (PVA) and then pressed into pellets 15 mm in diameter. For sintering, pellets were placed on three types of powder in an alumina crucible: a) Sb-doped BST powder (labelled as sample A); b) alumina powder (labelled as sample B) c) Sb, Mn - doped BST powder (labelled as sample C). All of the samples were sintered in an air atmosphere at 1350ºC, using heating and cooling rates of 5ºC/min. To examine any variability in the data, duplicate samples were sintered under the same conditions and two pellets from each experiment were selected for characterization.

Phase formation of polished surfaces in sintered samples was analyzed at room temperature using an X-ray diffraction technique (XRD), using CuKα radiation (Philips APD1700). The lattice parameters were calculated using a manual least square fitting method (Cullity, 2001). The microstructures of the as-sintered surfaces of samples were characterized using scanning electron microscopy (ESEM, Phillips XL30). The d.c. resistance change of the specimens as a function of temperature was measured using a digital multimeter (Agilent 34401A) and a suitable power supply; electrodes were applied using silver paste. The measurements were carried out from room temperature to ~ 320ºC using a silicone oil bath to heat the samples; a digital thermometer (Fluke S50) with a K-type thermocouple was used to monitor temperature.

Results and Discussion

XRD patterns for each sintered sample are shown in Figure 1. The tetragonal barium strontium titanate (BST) phase was indexed on the basis of the Joint Committee on Powder Diffraction Standards (JCPDS) data (JCPDS card, 2000). The *a* and *c* lattice parameters of all samples gave similar average values, $a = 3.972\pm0.005$ Å and $c = 3.994\pm0.005$ Å. However minor phases were present in all three samples. The d-spacings of these minor phases were consistent with phases previously identified with the aid of EPMA to be $(Ba,Sr)_6Ti_{17}O_{40}$ (with ~ 1 mol% Sr^{2+} for Ba^{2+} substitution) and $Ba_{1.95}Sr_{0.05}Ti_{1.2}Si_{1.8}O_8$ which segregate at intergranular regions (Bomlai *et al*., 2005).

The resistivities, ρ, of the samples as a function of temperature for the three different surrounding powders are potted in Figure 2; results are summarised in Table 1. All samples exhibited PTCR behavior with the T_C remaining constant at ~ 60ºC. There was little variation in room temperature resistivity (ρ_{RT}) for the different samples, with values of 162, 164 and 177 Ω cm for samples A, B and C respectively, whereas the maximum resistivity (ρ_{max}) showed a stronger dependence on surrounding powder, being highest for Sb-doped BST powder-beds, at 1.7×10^8 Ω cm (Table 1). The temperature of maximum resistivity (T_{max}) was about 256-258ºC when using Sb, Mn co-doped BST and Sb - doped BST powders, compared to (~ 302ºC) when alumina powder was used. The highest change of ratio ρ_{max}/ρ_{RT} was found to be about 10^6 for sample A, which is at least one order

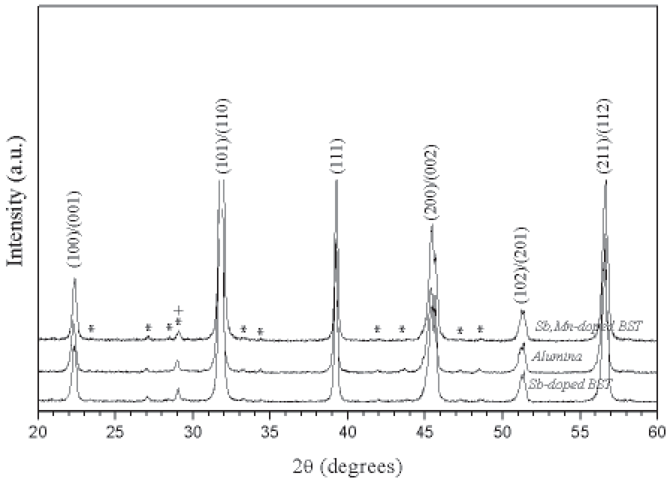

Figure 1. X-ray diffraction patterns of sintered ceramics showing phase formation with different surrounding powders during sintering; (+ = $(Ba,Sr)_6Ti_{17}O_{40}$ and * = $Ba_{1.95}Sr_{0.05}Ti_{1.2}Si_{1.8}O_8$).

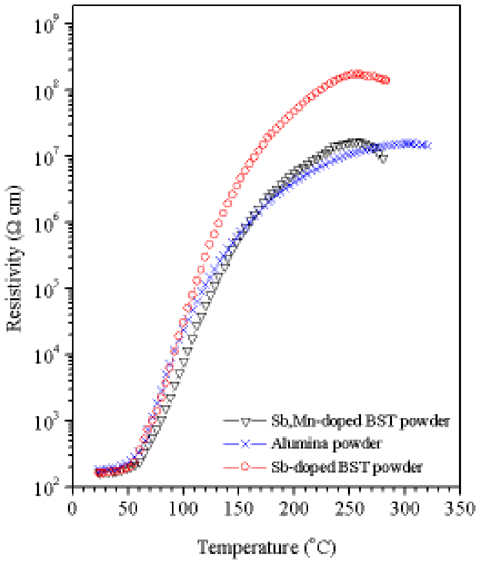

Figure 2. The resistivity-temperature characteristics of the samples for various surrounding powders during sintering at 1350ºC.

Table 1. Summary of values of room temperature resistivity (ρ_{RT}), maximum resistivity (ρ_{max}), the ratio ρ_{max} / ρ_{RT} and the temperature corresponding to ρ_{max} (T_{max}).

Samples	ρ_{RT} (Ω cm)	ρ_{max} (Ω cm)	ρ_{max} /ρ_{RT}	T_{max} (ºC)
A	162	1.73×10^8	1.07×10^6	258
B	164	1.67×10^7	1.02×10^5	256
C	177	1.53×10^7	8.64×10^4	302

of magnitude higher than for Samples B and C. The changes in electrical properties as a result of changing the placement powders is attributed to the vapours generated from the surrounding powder diffusing along grain boundaries in the BST sample pellets and changing their defect chemistry. The BST surrounding powder containing Sb_2O_3 and MnO_2 (Sample C) gave different results from the one with only Sb_2O_3 as additive (Sample A). As stated in the introduction it has been reported (Qi *et al.*, 2001) that an effective means of introducing Sb_2O_3 as a donor dopant for the purpose of creating A site vacancies on the ABO_3 perovskite lattice is to introduce antimony oxide through a vapour phase reaction. The surrounding powder in Sample C contained similar levels of Sb to Sample A but did not exhibit the increase in maximum resistivity values. However, this sample also contained MnO_2 as a co-additive (in the same ratio as in the BST pellet). Manganese acts as an acceptor dopant) and the oxide is also expected to exhibit volatility at the sintering temperature. Therefore the difference in PTCR data between Samples A and C infers that in Sample C both Mn and Sb vapours react with the BST pellet to give an overall neutral effect in terms of defect chemistry, and the properties are similar to BST pellets sintered on alumina used as a standard powder. The vapours are compensating for those lost from the pellets during sintering. In each of the samples the pellet surface in contact with the surrounding powder was removed by polishing before measuring the PTCR responses, therefore any solid state diffusion between alumina in contact with the BST pellets did not affect the PTCR results.

The microstructures of as-sintered surface of all samples are shown in Figure 3. The grains size distribution of sample A was rather uniform

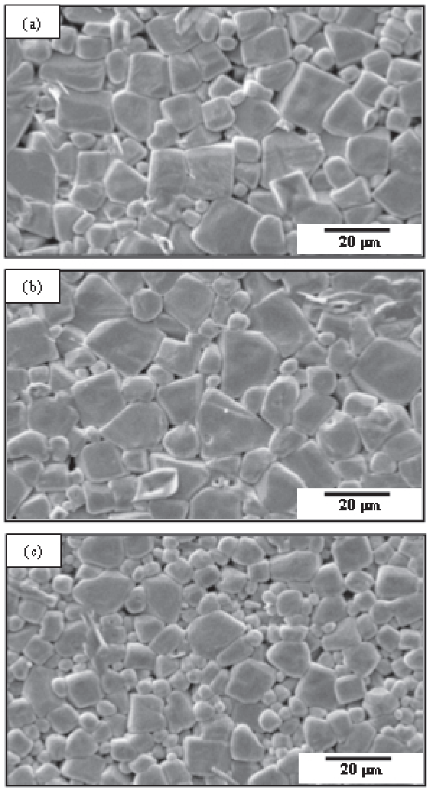

Figure 3. SEM micrographs of as-sintered surfaces of samples sintered at 1350ºC with different surrounding powders during sintering; (a) Sb-doped BST powder, (b) alumina powder and (c) Sb, Mn-doped BST powder.

and more equiaxed in shape than samples B or C. The samples differed slightly in grain size, all three sample-types exhibiting grains ranging in size from 5-20 µm. This result clearly shows that the surrounding powder significantly affects to grain size distribution, which is more obvious than grain size. It is suggested that the change in microstructure is a result of diffusing vapor along grain boundaries in BST samples.

The increase in resistivity in sample A also suggests that it results from the microstructure of the samples. It was previously reported that the uniform microstructure significantly affects the electrical properties (Bomlai *et al*., 2005) and performance of PTC devices. Additionally, a grain size distribution as homogeneous as possible and control heterophases between the grains are necessary for improvement of PTCR properties. Therefore, in this present work, the most uniform grain size of sample A resulted in the better PTCR characteristic than other samples.

Conclusion

The ceramics samples were prepared by a mixed-oxide method. During sintering process, the green samples were placed on different surrounding powders. Microstructural and PTCR behavior depended upon the powder, while crystal structure remained unaffected. The most uniform microstructure and six-orders of magnitude PTCR effect were obtained for samples using Sb-doped BST powder, which is at least one order of magnitude higher than for samples using alumina and Sb, Mn-doped BST powders. The changes in microstructure and electrical properties as a result of changing the placement powders was attributed to the vapours generated from the surrounding powder diffusing along grain boundaries in the BST sample pellets and changing their defect chemistry. Therefore, the PTCR effect is distinctly enhanced by using a suitable surrounding powder during sintering process

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