

FABRICATION OF POROUS Sb-DOPED BARIUM TITANATE CERAMICS USING SELF-ADHESIVE CARBON GRAINS FROM OIL PALM EMPTY FRUIT BUNCHES AS PORE-FORMING AGENT

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ABSTRACT

Self-adhesive carbon grains (SACG) from oil palm empty fruit bunches were used as pore-forming agent (PFA) in the fabrication of porous Sb-doped barium titanate (BaTiO_3) ceramics. Porous Sb-doped BaTiO_3 ceramics containing SACG were prepared by sintering mixtures of metal oxides at 1350°C for 2 hours in air. The effect of SACG addition on density, structure, microstructure, porosity and electrical resistivity of the porous ceramics produced was investigated. All the sintered ceramics showed a tetragonal structure, irrespective of the amount of SACG added. The porosity of the ceramics increased and the grain size decreased with increasing SACG contents. The prepared porous ceramics exhibit PTCR behavior in which the PTCR jump of the ceramics with SACG was about 10^4 which is higher than that of the ceramics without SACG. The increasing in the PTCR jump with increasing SACG content was attributed mainly to the increase in the electrical barrier height of grain boundaries and the porosity. It was found that the SACG is an effective PFA for fabricating porous BaTiO_3 -based ceramics.

Keywords: Self-adhesive carbon grains; Pore-forming agent; Sb-doped barium titanate;

INTRODUCTION

Ceramics based on barium titanate (BaTiO_3) have been extensively studied because such compounds possess many useful and interesting electrical properties. They have been widely utilized to manufacture many electronic components, such as multilayer capacitors, piezoelectric transducers, gas sensors and positive temperature coefficient thermistors [1, 2]. Porous semiconducting BaTiO_3 ceramics have been attracting interest and more favorable compared to dense BaTiO_3 ceramics because porous microstructure can form surface acceptor states and hence improve the electrical properties of the ceramics. For example, porous BaTiO_3 -based thermistors exhibit better heat resistance than dense ones and thus can be used as over current protectors in electric circuits [3]. In general, a number of routes have been employed to fabricate porous semiconducting BaTiO_3 . It can be prepared by thermal decomposition of barium tytanoyloxalate

BaTiO(C₂O₄)₂.4H₂O [4]. Another attractive alternative route, due to its simplicity and low cost, which nowadays become increasingly employ for fabricating porous BaTiO₃ is using pore-forming agent (PFA) prior to sintering. Many different kinds of additives can be used as PFAs such as polyethylene glycol [5], potato- and corn-starches [6, 7], and graphite [8, 9]. However, different PFAs promote porosity by different mechanism which in turn results in different effect in BaTiO₃ ceramics. Self-adhesive carbon grains (SACG) from pre carbonized fibers of oil palm empty fruit bunches is expected to have significant effects in the formation of pores in BaTiO₃ ceramics. SACG has been extensively used for fabricating porous carbon electrodes for supercapacitor [10, 11]. In the present paper we report the preparation and characterization of porous Sb-doped BaTiO₃ (referred to as Sb-BT) ceramics by using SACG as PFA. Sb-BT samples were prepared via solid state reaction at high temperature. Powders of Sb-BT were then mixed with various amount of SACG to produce porous Sb-BT ceramic samples. The samples were characterized to study the effect of SACG addition on their density, structure, microstructure, porosity and PTCR properties.

MATERIALS AND METHOD

The raw materials used to prepare the samples were BaCO₃ (Aldrich, 99.99% purity), TiO₂ (Aldrich, 99.99% purity), Sb₂O₃ (Fluka, 99.999% purity) powders and self-adhesive carbon grains (SACG, with powder size less than 106µm) from fibers of oil palm empty fruit bunches (EFB). The SACG powders used here were produced via a low temperature carbonization process of the pre-carbonized EFB based on the method developed by our group as described elsewhere [12]. Sb-BT ceramic powders were initially prepared by the conventional solid state reaction method using BaCO₃, TiO₂ and Sb₂O₃ powders as the starting materials. The Sb₂O₃ powder of 0.2 mol% was added into the mixture to produce n-type semiconducting ceramics. The starting materials were mixed in ethanol by ball milling for 12 hours in a jar using zirconia balls as grinding media. The ball-milled slurries were dried at 100°C in an oven for 1 hour. The dried powders were pressed into a green body and sintered at 1350°C for 2 hours in air. The sintered body was carefully ground in mortar and passed through a sieve to obtain Sb-BT powders with sizes less than 32µm. The different amount of SACG (1 to 20 weight percent) was added to the as-sintered Sb-BT powders to produce porous Sb-BT ceramic samples. The mixture of Sb-BT and SACG powders were ball-milled for 12 hours using the zirconia balls. The resulting mixed powders were then pressed in a mould by applying a compression pressure of 5 metric tones to prepare pellets of about 13 mm in diameter and 2 mm thick. The weight of each pellet was fixed to about 1 g and a total of six pellets, designated as samples A to F, were prepared. The green pellets were heated at 1350°C for 1 hour in air with a heating rate of 3°C per min and cooling rate of 3°C per min to 300°C and the furnace cooled to room temperature.

The experimental density of the green bodies and the sintered ceramic pellets were determined from the measurement of their weight and dimension. The crystalline structure of the ceramic sample was analyzed with X-ray diffraction (XRD) (Bruker AXS model D8 Advance) using Cu-K_{α1} with wavelength of 1.5406Å. The

microstructure was examined using a scanning electron microscope (FESEM) (SUPRA 55VP). The average grain size of the sintered ceramics was estimated using the line intersecting method. Electrical resistance was measured using a digital multimeter (MITOYO Digimatic Caliper Series-500) in air from room temperature to 250°C with a heating rate of 10°C per min.

RESULTS AND DISCUSSION

The weight, dimension and density of the green pellets and the sintered pellets of the Sb-BT ceramics containing various amounts of SACG are tabulated in Table 1. The results show that the green pellets lost the weight and volume after being converted into the sintered pellets which mainly due to the release of non-carbon contents from SACG and rearrangement of atoms during the heating process. SACG contents about 50% C, 43% O₂, 6% H₂ and 1% N₂ which exist in the form of inorganic-based compounds [12]. During heating at high temperature (>1000°C), those compounds decomposed into volatile compounds and were liberated from the ceramic body.

Tanle 1: Weight, dimension and density of the green pellets (GP) and sintered pellets (SP) of Sb-doped BaTiO₃ ceramics containing SACG

Sampel	SACG Content (wt.%)	GP				SP			
		w (g)	d (mm)	t (mm)	ρ (gcm ⁻³)	w (g)	d (mm)	t (mm)	ρ (gcm ⁻³)
A	0	0.9706	13.256	1.584	4.264	0.8761	12.798	1.462	4.658
B	1	0.9893	13.456	1.782	3.904	0.8846	12.783	1.492	4.619
C	5	0.9558	13.504	1.718	3.884	0.9016	12.730	1.564	4.529
D	10	0.9343	13.560	1.728	3.744	0.8443	12.384	1.538	4.244
E	15	0.9498	13.566	1.934	3.398	0.8639	12.484	1.760	4.008
F	20	0.9702	13.580	2.172	3.084	0.7756	12.418	1.882	3.403

The density values of the sintered Sb-BT ceramic pellets with SACG content (samples B to F) are much lower than the density of the pellet without SACG (sample A). This difference is due the formation of pore in the pellet cause by the burning-out of SACG during sintering. It is also found that the density of the Sb-BT pellets decreased with increasing SACG content due to the increase in pore formation in the ceramics.

Figure 1 shows the XRD profiles for the prepared Sb-BT ceramic samples without and with SACG addition. The results show that only BaTiO₃ peaks present for all samples which reveal that these ceramics are single phased. The lattice parameters calculated for all the samples showed that the samples have a tetragonal perovskite structure, irrespective of the added SACG content, with the values of a \approx 3.992 Å and c \approx 4.031 Å. A slight change in the values of lattice parameters a and c among the samples is due to the substitution of Ba²⁺ by Sb⁵⁺. The ionic radii of Ba²⁺, Ti⁴⁺ and Sb⁵⁺ are 1.29 Å, 0.90 Å and 1.36 Å, respectively, and the atomic radius of the carbon atom is 0.77 Å [8, 13].

The XRD profiles also show that the peaks of samples containing SACG shifted toward lower angles as compared to the peaks of sample without SACG. This suggests that the carbon atoms from the added SACG are present on interstitial sites in the BaTiO₃ lattice to form interstitial solid solutions as was reported for the porous BaTiO₃ ceramics added with graphite [8].

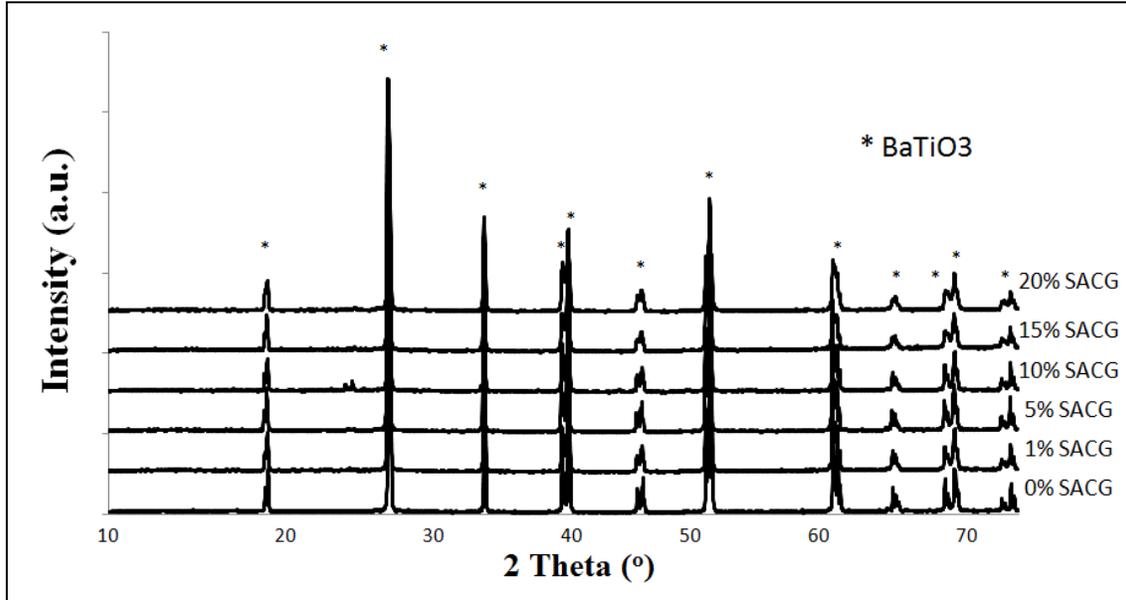


Figure 1: XRD patterns of the Sb-doped BaTiO₃ containing SACG

Table 2 shows the porosity and grain size of the sintered Sb-BT pellets. It is found that the porosity increased and the grain size decreased with increasing SACG content. The porosity obtained is about similar percentage with those reported earlier [6-8]. The increase in porosity with increasing SACG content is believed to be due to an enhanced evolution of carbon monoxide and carbon dioxide gases associated with exothermic reactions during sintering process [14]. Pores in the porous ceramics cause oxygen to be easily absorbed at the grain boundaries and to form surface acceptor states. The formation of pores and the increase of porosity in the ceramic samples with the increasing SACG content can be explained by the fact that the cavities, which are formed due to the burning out of non-carbon content from the SACG during sintering, act as the sites for pore generations.

Table 2: Porosity and grain size of the Sb-doped BaTiO₃ containing SACG

Sample	SACG Content (wt%)	Porosity (%)	Grain Size (µm)
A	0	23.4	5.0 - 36.0
B	1	24.1	4.0 - 34.0
C	5	25.5	3.0 - 23.0
D	10	30.2	3.0 - 17.0
E	15	34.0	2.0 - 15.0
F	20	44.0	1.0 - 12.0

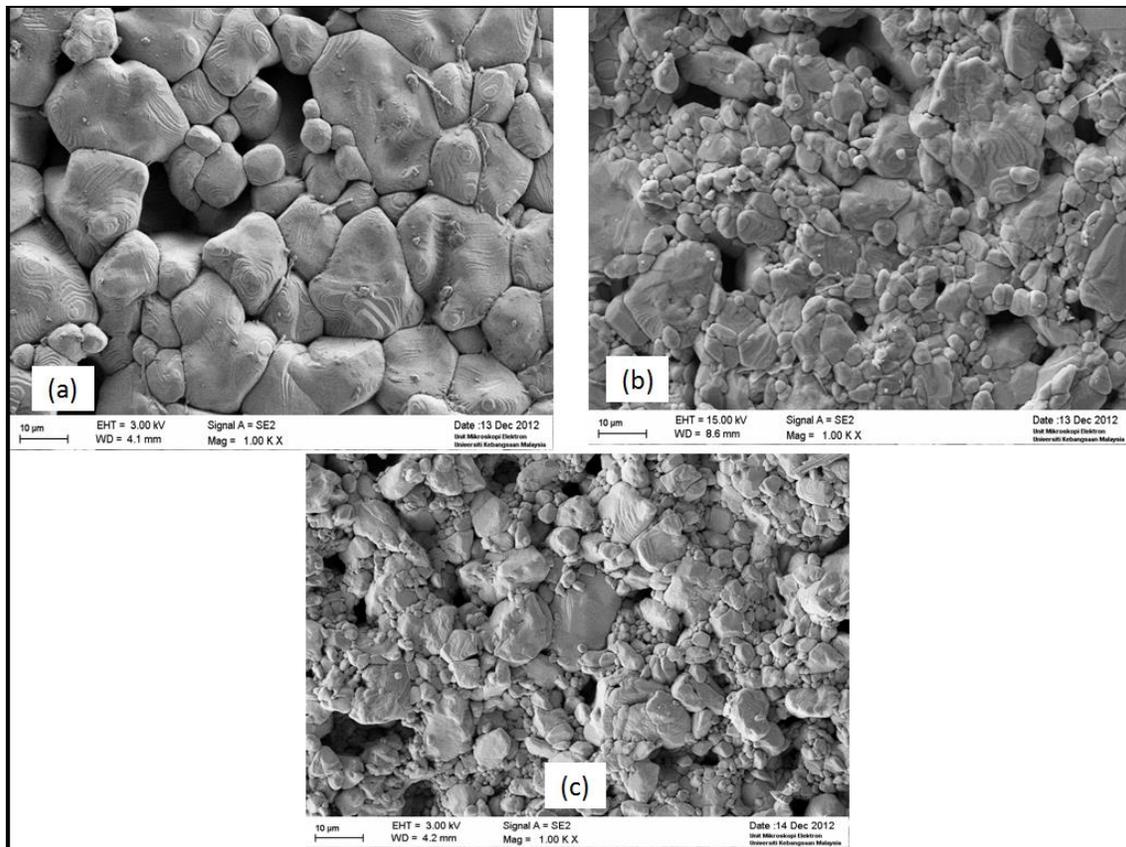


Figure 2: SEM micrographs of the Sb-doped BaTiO₃ samples (a) A (0 wt.% of SACG), (b) C (5 wt.% of SACG) and (c) D (10 wt.% of SACG)

The SEM images of the surfaces of samples A (without SACG), C, and D obtained at magnification of 1000x are shown in Figure 2. As can be observed from the images, distinct pores and grain sizes were formed in different samples resulting from the addition of SACG. In general, the microstructures show that grain sizes of the Sb-BT sample without SACG are bigger than that of the samples with SACG. It is also shown

that the grain sizes of the samples decreased and the pore sizes increased with the increasing SACG content. For example, the average pore sizes of the Sb-BT with 5 wt.% and 10 wt.% of SACG were 23.71 μm and 25.14 μm , respectively. These results confirm the porosity study as discussed above and also similar with the results observed in the porous BaTiO_3 which were added with corn and potato-starches [6, 7].

The electrical resistivity measured in air from room temperature to 250°C for the Sb-BT samples containing various amount of SACG is shown in Figure 3. As expected, the Sb-BT ceramic samples exhibited PTCR characteristics where the resistivity of the ceramics abruptly increases above Curie temperature ($\sim 110^\circ\text{C}$). It is found that the PTCR jump ($\rho_{\text{max}}/\rho_{\text{min}}$) was slightly increased with the increasing SACG content. The value of PTCR jump for the samples with SACG was around 10^4 which are about two orders higher than the sample without SACG. This is believed to be attributed from the pore formation in the ceramics and can be explained based on the grain boundary electrical barrier model as was proposed by Heywang [13]. The presence of pores in the ceramics can cause the grain boundaries to be easily oxidized and consequently affect the electrical barrier height of grain boundaries. As the amount of SACG increases, the porosity increases resulting in the increase of the electrical resistivity of grain boundaries in the ceramics due to the increase in electrical barrier height, which results from the adsorption of chemisorbed oxygen atoms at the grain boundaries. As a result, the resistivity of the Sb-BT ceramics increases with the increasing SACG content. This variation may also be attributed from the changes in the donor concentration of grains and the grain size. In addition, the results in Figure 3 also show that the resistivity at room temperature of the Sb-BT with SACG is higher than that of the Sb-BT ceramic sample without SACG, and slightly increased with increasing addition of SACG. This is also attributed from the effect of porosity as well as the semiconducting grains.

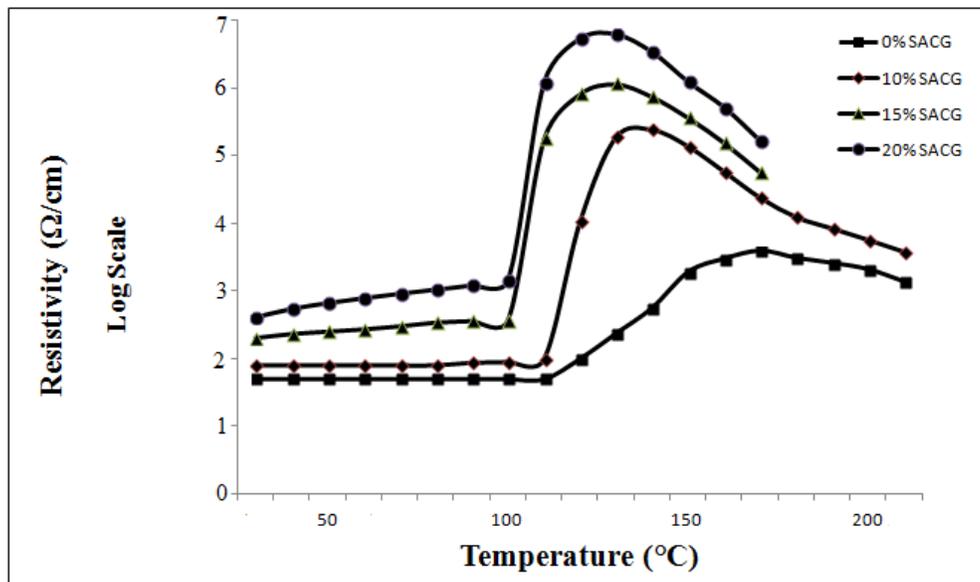


Figure 3: Electrical resistivity as a function of temperature for the Sb-doped BaTiO_3 containing SACG

Based on the results obtained from this study it is clearly shown that SACG is an effective PFA for fabricating porous Sb-BT ceramics. Further study on the effect of SACG on the properties of porous Sb-BT ceramics such as complex impedance analysis to determine the electrical properties of grain boundaries and donor concentration of grains of the ceramics as well as their gas sensing properties will be carried-out.

CONCLUSIONS

Porous Sb-doped BaTiO₃ ceramics were successfully fabricated by adding SACG. The addition of SACG as pore-forming agent gave rise to porous ceramics with smaller grain sizes of 1.0 – 34.0 μm. As the content of SACG increased, the porosity and pore size increased and the grain size slightly decreased. From the XRD results, it was found that only BaTiO₃ peaks appeared in the Sb-doped BaTiO₃ ceramics with and without SACG. The porous Sb-doped BaTiO₃ exhibits PTCR behavior in which the PTCR jump increased with increasing content of SACG due to the increase in the electrical barrier height of grain boundaries and the porosity as well as the decrease in the donor concentration of grains and grain size. The results showed that SACG is an effective pore-forming agent for preparing porous BaTiO₃ ceramics. The porous ceramics produced in this work are potential candidates as gas sensor and high-performance porous materials.

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