

Self-propagating solid state routes to BaSnO₃; investigation of gas sensing properties

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Thermal initiation of mixed powders of a tin source (Sn, SnCl₂, SnO₂) and barium peroxide in air produce a self propagating high temperature synthesis (SHS) wave of velocity 2–5 mms⁻¹ and temperature 950–1050°C. The product from the reaction is predominantly BaSnO₃ with some SnO₂ and Ba₂SnO₄ impurities. Annealing of the SHS powders at 1000°C for 2–72 h forms phase pure cubic BaSnO₃, $a = 4.116(3) \text{ \AA}$. X-ray photoelectron spectroscopy showed the expected Ba: Sn: O ratios with binding energy shifts for Ba 3d_{5/2} at 775.8 eV; O 1s at 526.1 eV and Sn 3d_{5/2} at 482.7 eV. Scanning electron microscopy showed ca 0.5 μm agglomerates of cubic crystallites of dimension 0.15 μm, whilst energy dispersive analysis by X-rays showed the expected barium to tin ratios. Infra-red spectra of the annealed products were equivalent with commercial samples. The SHS prepared barium stannates were good sensors for carbon dioxide, showing n-type response.

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1. Introduction

Barium stannates have useful dielectric properties that have been used in capacitors and ceramic boundary layers [1]. These materials also show considerable promise as gas phase sensors for the detection of carbon monoxide [2] and carbon dioxide [3]. Three phases in the BaO–SnO₂ phase diagram have been reported; BaSnO₃, Ba₂SnO₄ and Ba₃Sn₂O₇ [4]. The BaSnO₃ phase is the most technologically important, however it is somewhat difficult to synthesise. Traditionally it is made at 1200°C by the solid state reaction of BaCO₃ and SnO₂. This procedure suffers from significant impurities and large irregular grain sizes [4]. One of the main synthetic challenges is the removal of the phase Ba₂SnO₄ [5]. This can be particularly problematic as non-stoichiometry is supported in the structure through the formation of alternating layers of the perovskite BaSnO₃ and rock salt BaO along the *c*-direction [5]. Alternative routes to BaSnO₃ have employed hydrothermal techniques [6] and precipitation synthesis [7]. These methods are at lower temperature but are complicated by the co-formation of SnO₂ which has proved difficult to remove.

We have an interest in forming solid state materials by innovative solid state routes. These have included Self propagating High temperature Synthesis (SHS) and a newer variant called solid state metathesis reactions [8]. These solid state reactions are self energetic, proceed by a solid-flame (synthesis-wave) and are accompanied by rapid heating and cooling. These techniques often form products with different morphologies and particle size distributions compared to traditional synthesis. In

particular the as made SHS products have lower density and higher porosity than conventionally prepared material. One of the main focal points of this work has been the synthesis of mixed-metal oxides. Traditional SHS synthesis of oxide powders normally requires the use of special reactors and oxygen atmospheres. We have shown that barium peroxide, which on decomposition forms oxygen can be a useful internal oxidising agent and allows the synthesis of metal oxides in air. In particular we have used this methodology to form barium ferrite and barium titanate powders [9].

In this paper we investigate a number of alternative pathways to BaSnO₃ via SHS reactions in air, and give a preliminary report on the materials gas-sensing properties.

2. Experimental procedure

All reagents were of 99.9% purity or better and purchased from Aldrich Chemical Co. and used without further purification. Barium nitride was prepared by the reaction of nitrogen and barium in molten sodium by Dr M. Barker at Nottingham University. Commercial synthetic air (79% N₂, 21% O₂, BOC) was used for the gas resistance measurements. Manipulations and weightings were carried out in air. X-ray powder diffraction patterns were determined on a Siemens D5000 transmission powder diffractometer using germanium monochromatic Cu K_{α1} radiation ($\lambda = 1.5406 \text{ \AA}$). SEM/EDAX was determined on a Hitachi SEM S-570. Electron probe analysis were conducted on a Jeol EMA using polished samples and compared to metal standards. XPS measurements were

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TABLE I X-ray powder diffraction data of the products from the SHS reactions of Barium and barium peroxide with tin oxides, chloride and metal

Synthesis method	Phase identified	Cell type	Observed lattice parameter (+/-0.003 Å)	Literature lattice parameter ⁶ /Å
BaO ₂ + Sn + SnO ₂	BaSnO ₃	Cubic	<i>a</i> = 4.115	<i>a</i> = 4.116
BaO ₂ + Sn	BaSnO ₃	Cubic	<i>a</i> = 4.116	<i>a</i> = 4.116
BaO ₂ + SnCl ₂	BaSnO ₃	Cubic	<i>a</i> = 4.114	<i>a</i> = 4.116
Ba + SnO ₂	BaSnO ₃	Cubic	<i>a</i> = 4.116	<i>a</i> = 4.116
BaCl ₂ + SnO ₂	BaSnO ₃	Cubic	<i>a</i> = 4.117	<i>a</i> = 4.116
BaO ₂ + SnO ₂	BaSnO ₃	Cubic	<i>a</i> = 4.117	<i>a</i> = 4.116
Ba ₃ N ₂ + 3 SnO ₂	BaSnO ₃	Cubic	<i>a</i> = 4.120	<i>a</i> = 4.116

Products were sintered after SHS for between 2–72 h at 1000°C prior to measurement.

performed with a VG ESCALAB 220i XL using focused (300 μm spot) monochromatic Al-K_α radiation at a pass energy of 20 eV. Scans were acquired with steps of 50 meV. A flood gun was used to control charging and the binding energies were referenced to an adventitious C1s peak at 284.8 eV. Infra-red spectra were recorded on a Nicolet 205 spectrometer using KBr pressed discs. Powder X-ray diffraction patterns were indexed using TREOR or METRIC-LS programmes, and referenced against an external data base. Resistivity and gas sensitivity measurements were obtained using a KEITHLEY autoranging multimeter at 60 second intervals. The samples were pressed into pellets (1 tonne pressure) and sandwiched between gold electrodes. The electrodes were 13 mm in diameter, pressed onto the pellets and held in place by a clamp device using alumina spacers. Pellets typically contained 200 mg of powder and were 1 mm thick, 13 mm diameter with ca density of 2 g cm⁻³. Gas flow and concentration was controlled via mass flow controllers. Measurements of gas response as a function of temperature were also obtained by either exposing the samples to 1000 ppm of carbon dioxide in synthetic air for 10 minutes every twenty minutes or by exposure to different CO₂ concentrations for 50 minutes. Runs were obtained only in zero relative humidity. The measurements were initiated at 100°C and taken to 700°C over a period of 10 hr and brought back to the initial temperature over an iden-

tical period of time. Measurement of gas response as a function of gas concentration was obtained by stabilising samples at 700°C for 6 h and then exposing the samples to increasing concentrations of carbon dioxide in air. The concentrations of carbon dioxide were taken to be 200, 400, 800 and 1000 ppm. The sample was then taken to 400°C and the same concentrations of CO₂ applied to the sample.

2.1. Preparation of BaSnO₃

In all reactions a 1:1 stoichiometric ratio of barium to tin was used in the starting mixture. Reagents were ground together in an agate pestle and mortar under a nitrogen atmosphere. Reactions were initiated in air using a nichrome wire filament (850°C), this produced in most cases a propagation wave (2–5 mm s⁻¹) (Table I). The resulting powders were sintered in an aluminosilicate ceramic boat at 1000°C for between 2–72 h. Reactions that failed to propagate via filament were still annealed. The samples were analysed by X-ray powder diffraction (Table I), SEM/EDAX, XPS, FT-IR and resistivity measurements under different gaseous atmospheres.

3. Results

Reaction of various barium and tin reagents under SHS conditions produced BaSnO₃. This is shown in the idealised equations 1–7. The initial SHS products showed

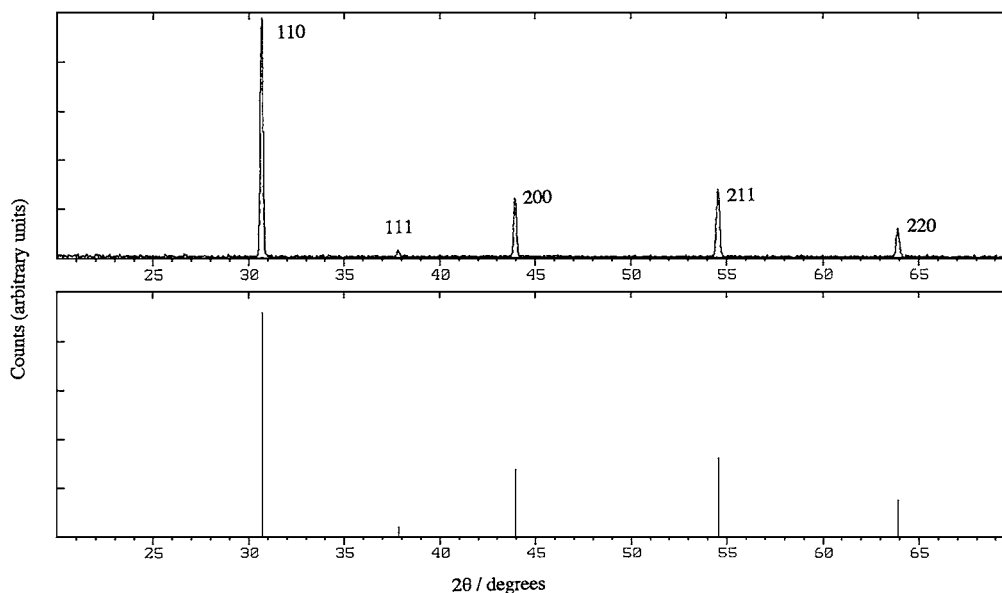
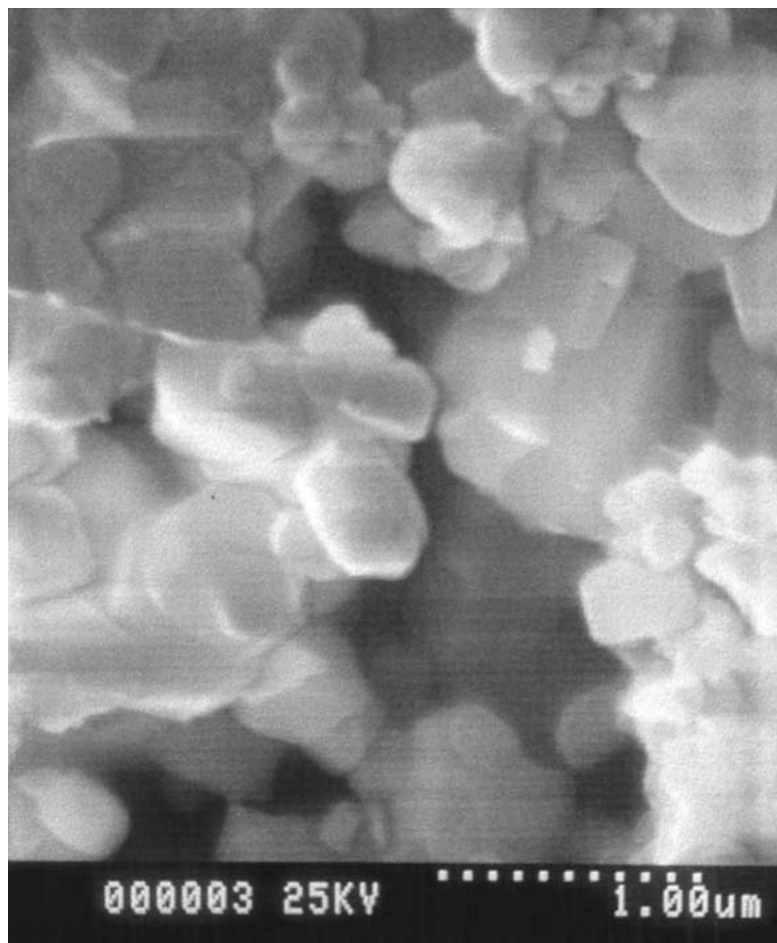
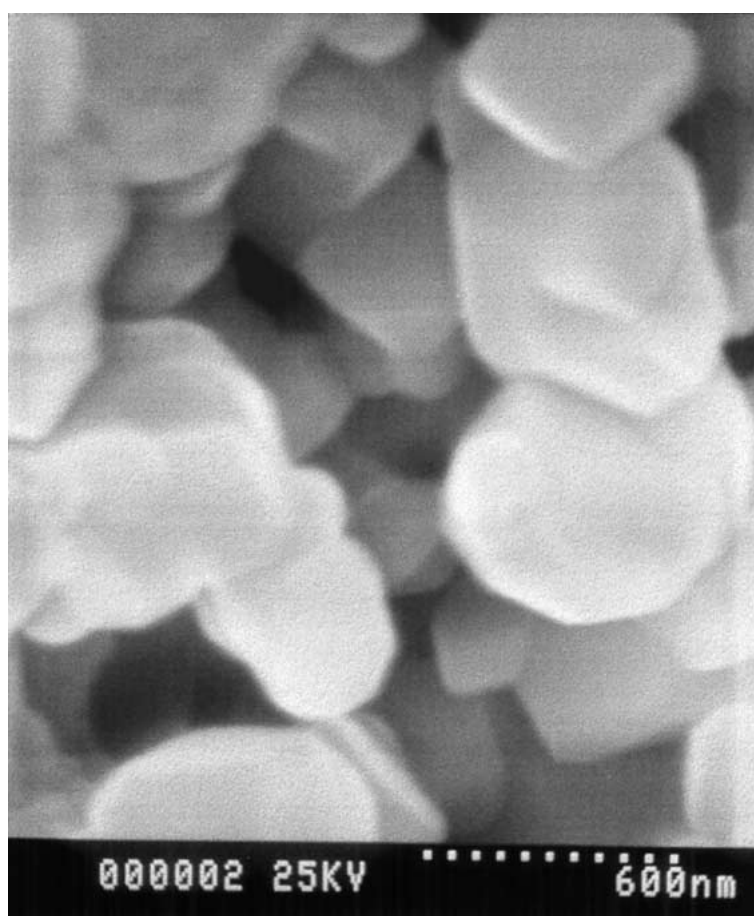


Figure 1 Top trace; X-ray powder diffraction pattern obtained from the reaction of BaO₂, Sn and SnO₂ after annealing at 1000°C for 12 h. Bottom trace; literature X-ray powder diffraction stick pattern for BaSnO₃.



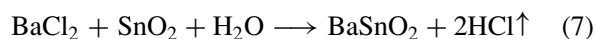
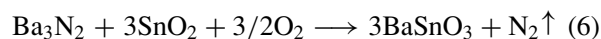
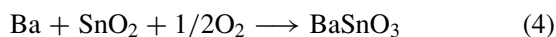
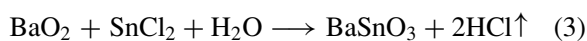
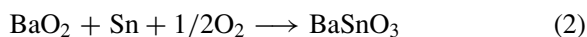
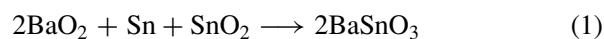
(a)



(b)

Figure 2 (a) Scanning electron micrograph of BaSnO₃ prepared from the SHS reaction of BaO₂, Sn and SnO₂ after annealing at 1000°C for 12 h. (b) Scanning electron micrograph of BaSnO₃ prepared from BaCO₃ and SnO₂ 1200°C/48 h, three cool and grind stages (conventional preparation).

in some cases partial reaction and formation of minor amounts of SnO_2 and Ba_2SnO_4 . Sintering of the SHS prepared powders at 1000°C for 2–72 h produced in most cases phase pure BaSnO_3 . Yields in all reactions were essentially quantitative, the only losses were due to mechanical handling.



All of the reactions proceeded in the propagation mode, spreading out from the point of ignition with a yellow-orange solid flame ($950\text{--}1050^\circ\text{C}$) of velocity $2\text{--}5\text{ mm s}^{-1}$ with the exception of Equations 5 and 7 which failed to propagate. SHS reactions typically involve simultaneous oxidation and reduction reactions [9]. In the reactions detailed in Equations 1–3 the tin metal or tin dichloride is oxidised and oxygen is reduced. The tin or tin dichloride acts as the fuel source. Addition of SnO_2 to the reaction mixtures acts as a heat-sink to reduce the overall reaction temperatures whilst the barium peroxide acts as an internal intimately mixed source of oxygen. Most SHS reactions used for the formation of complex oxides involve the use of special reactors and oxygen gas to promote the reaction; notably most of the reactions studied here propagated in air. Combination of BaO_2 and SnO_2 would not propagate in the SHS mode because no reducing agent was present, however these powders did react on heating to 1200°C for 72 h to form predominantly BaSnO_3 .

The products (Equations 1–7) were analysed by X-ray powder diffraction, SEM/EDAX, FT-IR, XPS and gas sensing measurements. The X-ray powder diffraction patterns of the sintered material showed phase pure BaSnO_3 , Table I, Fig. 1. The material indexed with a parameters equivalent to literature measurements. The unsintered powders showed predominantly BaSnO_3 with some amounts of SnO_2 and Ba_2SnO_4 . This correlates with the conventional synthesis reported by Gallagher and Johnson [10] where the intermediates Ba_2SnO_4 and SnO_2 were isolated. Although SHS reactions are inherently different to conventional ceramic synthesis, in these reactions they seem to follow the same mechanistic behaviour with the pre-sintered material containing similar Ba_2SnO_4 and SnO_2 impurities.

The sintered materials showed only barium and tin by EDAX (oxygen was below the machine threshold) in the expected 1:1 ratio across many surface spots. SEM showed ca $0.5\text{ }\mu\text{m}$ agglomerates of cubic crystallites of approximate size $0.15\text{ }\mu\text{m}$, Fig. 2. The XPS of sintered BaSnO_3 showed the elements in the expected ratios (Ba 20: Sn 20: O 60), the barium $3d_{5/2}$ peak was centred at 775.8 eV , the O 1s at 526.1 eV and the Sn $3d_{5/2}$

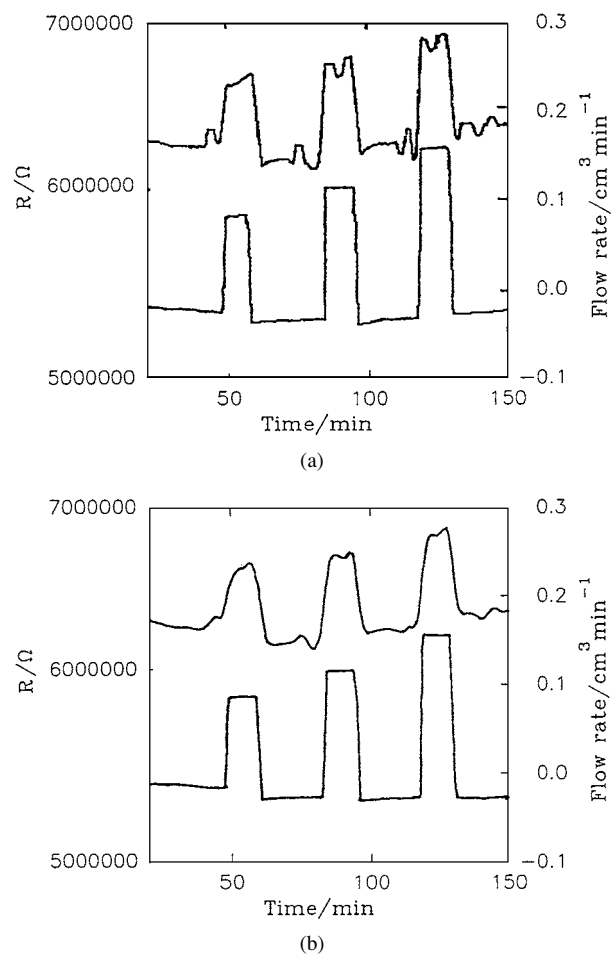


Figure 3 (a) Electrical resistance (ohms) and CO_2 flow rate (y-axis) against time for SHS prepared BaSnO_3 . Top trace shows the change in resistance of BaSnO_3 , bottom line shows variation in CO_2 flow rate in $\text{cm}^3\text{ min}^{-1}$ in air (11 min^{-1}). (b) Electrical resistance (ohms) and CO_2 flow rate (y-axis) against time for commercial BaSnO_3 . Top trace shows the change in resistance of BaSnO_3 , bottom line shows variation in CO_2 flow rate in $\text{cm}^3\text{ min}^{-1}$ in air (11 min^{-1}).

at 482.7 eV . These binding energy shifts are consistent with formation of BaSnO_3 [10]. The FT-IR spectra of sintered BaSnO_3 was identical to standard material (Aldrich Chemical Co).

The CO_2 sensing properties of SHS barium stannate (as prepared in Equation 1) were compared to conventionally prepared material (BaCO_3 , SnO_2 $1200^\circ\text{C}/48\text{ h}$, 3 cool and grind stages). Both materials showed marked changes in resistance with CO_2 concentration, the SHS material mirrored the conventionally prepared material and showed n-type response with increasing CO_2 concentration (Fig. 3 a and b). Both the commercial samples and the SHS sample showed a rapid response to pulses of CO_2 in dry air. The gas response was greatest to low concentrations of CO_2 ; exposure to increasing CO_2 concentrations for 50 minutes did cause a change in resistance (Fig. 4 a and b).

4. Discussion

The SHS syntheses are relatively easy to perform. The driving force in the reactions is the oxidation of tin metal or tin(II) chloride (580 kJ mol^{-1}). These reactions are sufficiently exothermic to proceed in the propagation mode (solid flame), in air, without recourse to oxygen. This is in part a consequence of the presence of

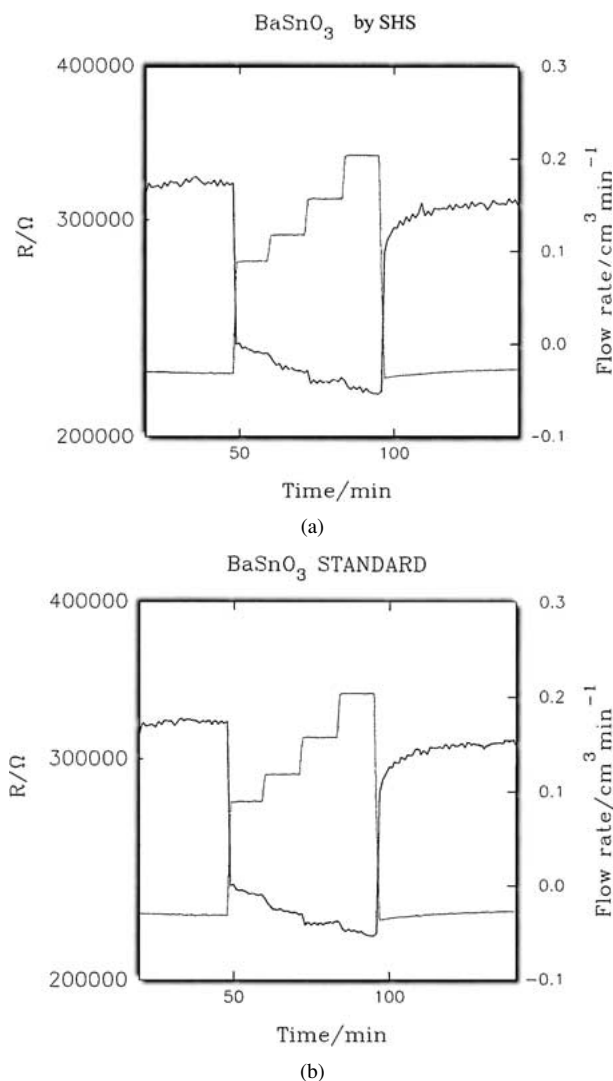


Figure 4 (a) Electrical resistance (ohms) and CO₂ flow rate (y-axis, smooth line) against time for SHS prepared BaSnO₃ (reaction 1). (b) Electrical resistance (ohms) and CO₂ flow rate (y-axis, smooth line) against time for commercial BaSnO₃.

barium peroxide which decomposes to form oxygen gas and helps the synthesis wave propagate through the solid. The as-made product from the SHS synthesis is predominantly crystalline BaSnO₃, however the product is contaminated with some unreacted starting material and Ba₂SnO₄. The SHS as-made solids are, however, very sinter-active and readily form single phase BaSnO₃ at 1000°C. BaSnO₃ made by these new routes shows sub-micron cubic crystallites with good changes in resistance with carbon dioxide concentration. However the responses to CO₂ are equivalent to those observed from conventionally prepared material. It is not immediately obvious that the SHS prepared materials have any immediate advantages compared to commercial material. In terms of gas response they are

virtually equivalent; the SHS materials are somewhat easier to form than conventional material as they do not require frequent firing and grinding stages during synthesis.

5. Conclusions

SHS reactions offer alternative routes to BaSnO₃ that are rapid and somewhat easier to perform than traditional precipitation-thermolysis routes. The products after sintering are equal in purity to traditionally made materials and show equivalent gas sensitivity to CO₂. The SHS prepared materials offer little real functional advantage over commercially made materials except that the synthesis is slightly easier. We anticipated that SHS might produce a completely new BaSnO₃ microstructure as SHS tends to form very porous solids. However the initial SHS synthesis in all reactions did not form phase pure BaSnO₃. This required the products to be sintered so that a single phase material was obtained. Unfortunately, although the sintering of the SHS product was rapid, it destroyed the SHS engineered microstructure. This led to gas response characteristics equivalent to commercial material.

Acknowledgements

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