Characterization of BaSnO$_3$-based ceramics
Part 1. Synthesis, processing and microstructural development

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Abstract

The compound BaSnO$_3$ together with its Ca- and Sr-analogs, has recently been projected as potential electronic ceramic material (thermally stable capacitor, chemical sensor for humidity, CO and NO$_x$, etc.). In order to fill the information gaps in the reported research, a vigorous and systematic investigation on these exotic materials has been initiated. A thorough study of BaSnO$_3$ with respect to its synthesis, processing and microstructural characterization has been made. In order to establish a standard methodology for low-cost mass-manufacturing with identical and beneficial microstructure and reproducible electrical characteristics, different synthesis routes (solid-state and self-heat-sustained) were adopted. Evolution of microstructure which is intimately related to the envisaged properties in the ceramics, was closely and systematically followed in terms of sintering over a wide range of temperatures and soak time. This communication forms the first of two parts in a series of investigations on Mn$_3$O$_5$ systems, where results on the synthesis and processing of “phase pure” barium stannate (BaSnO$_3$) and development of interesting microstructure are presented. © 1998 Elsevier Science S.A.

Keywords: Barium stannate; Capacitor; Gas sensor; Electronic ceramics; Solid-state; Self-heat-sustained; Microstructure

1. Introduction

The double oxides of the general formula, (AE)BO$_3$, formed between the oxides of alkaline-earth metals (AE = Ca, Sr and Ba) and those of some of the group IV elements are of great industrial and technological importance. For instance, the AE carbonates are the well-known precursors to innumerable inorganic syntheses and reactions, while AE silicates are of relevance and direct bearing in the slag chemistry of industrial production of iron and steels. Similarly, the discovery of superconductivity in “copper-free” cubic perovskite systems such as Ba$_{1-x}$Pb$_x$SbO$_3$ ($T_c=3.5$ K at $x=0.25$) and BaPb$_{1-x}$Bi$_x$O$_3$ ($T_c=13$ K at $x=0.3$) [1] has triggered much activity in the pseudobinary alkaline-earth oxide–PbO(PbO$_2$) systems. In addition, the technological impact of closely structure-related titanates of the alkaline-earth metals is too great to be ignored, of which BaTiO$_3$ (piezoelectric) and SrTiO$_3$ (varistor) are the most important electroceramics [2–4].

Barium stannate, BaSnO$_3$, belongs to the family of analogous alkaline-earth stannates (Mn$_3$O$_5$, where M = Ca, Sr and Ba) which are currently being pursued for their attractive dielectric characteristics, finding application as thermally stable capacitors in electronic industries. In pure as well as in doped forms these stannates have also been investigated as potential sensor materials for a host of gases, including CO, HC, H$_2$, Cl$_2$, NO$_x$ and humidity [5–9]. There is great scope for exploiting heterojunctions of these stannates with other suitable oxides as capacitive sensors for carbon dioxide detection and metering [10]. Recently, Ostrick et al. [11] have reported results of Hall measurements on BaSnO$_3$ at high temperatures to elucidate the nature of defects prevailing in the material. It has been reported that barium stannate has a band gap of 3.4 eV [12], which is well within the range of 3–3.5 eV, generally desired for gas sensor materials [13]. Suggestions have also been made that, by combining BaTiO$_3$ with BaSnO$_3$ (BTS), multifunctional ceramic sensors can be developed which can detect temperature, relative humidity, and gases such as prozylene, acetylene and ethylene at ambient temperatures and pressures [14].

Despite such technological importance, these stannates have not been as thoroughly and systematically studied as the corresponding titanates. For example, no sound and reliable data is available on the thermodynamic stability of these compounds or on other compounds in the AO–SnO$_2$ pseudobinary systems. Such data is invaluable since it will assist in detecting and delineating any phase-field shifts.
that could occur at moderate to high temperatures owing to
the pronounced volatility of SnO (disproportionation product
of SnO$_2$). Surprisingly, only a partial phase diagram is
available on the BaO–SnO$_2$ system in the literature [15];
no phase diagrams have been reported for the Ca and Sr
analogs. In addition, while the BaO–SnO$_2$ phase diagram
shows the existence of only one compound, viz. BaSnO$_3$
(Ba:Sn=1:1), reliable JCPDS cards are available for compo
ounds such as Ba$_3$Sn$_2$O$_7$ and Ba$_4$SnO$_4$ (with Ba:Sn =
1:0.67 and 1:0.50, respectively). Moreover, any informa
tion on processing and evolution of microstructure in
these materials and their impact on the electrical charac
teristics is also lacking in the literature. Smith et al. [16]
have prepared BaSnO$_3$ by solid-state method using stoichiometric amounts of BaCO$_3$ and SnO$_2$ and heating at
1200°C for 16 h. The compound was then reground,
pelletized and annealed in air at 1300°C for 43 h. The
compound was indexed as having a cubic perovskite
structure with the lattice parameter $a=4.119$ Å. Antimony
sesquioxide doped-BaSnO$_3$ with the formula BaSn$_{0.85}$Sb$_{0.15}$O$_3$ were also synthesized by Smith et al. in
a similar fashion using BaCO$_3$, SnO$_2$ and Sb$_2$O$_3$. The
mixtures were heated at 1200°C for 16 h followed by
annealing at 1500°C for 65 h. However, antimony sesqui
oxide is a low melting compound ($T_m=656^\circ$C) and is
known to have pronounced volatility even at moderate
temperatures (cf. 16.1 mm Hg at 500°C). In the light of
reliable thermodynamic data, Sb$_2$O$_3$ has a vapor pressure of
308.6 mm Hg above the liquid at 1200°C [17]. With this
rather significant magnitude of vaporization of Sb$_2$O$_3$ at
the working temperature, synthesis of the targeted com
 pound is not likely to be achieved. Bao et al. [18] had
prepared BaSnO$_3$ via coprecipitation from solution con
taining BaCl$_2$ and SnCl$_2$, using oxalic acid as the precipi
tating agent in the presence of water. However, a sintering
temperature of 1000°C only was employed. Recently,
Upadhyay et al. [19] have reported solid-state synthesis of
BaSnO$_3$, using BaCO$_3$ and SnO$_2$ as the starting material.
The calcination was done at 1200°C for 6 h and sintering at
1250–1400°C for times ranging between 6 to 12 h. The
only micrograph shown by these authors exhibited a
significant amount of porosity with poor grain-to-grain
connectivity. It is also difficult to make out the presence of
gains with cubic morphology in the micrograph as
claimed by the authors.

Contrary to these investigations [16,18,19], it was found
in the present work (see the subsequent sections) that
sintering in the range of 1200–1400°C was inadequate for
proper grain growth, intergranular connectivity and
adequate densification of BaSnO$_3$. This aspect is important
since, in order to make a capacitor component out of
BaSnO$_3$, the material is required to be essentially “pore-
free”, since pores would act as sink to the electrical charge
carriers and would be the source of poor grain-to-grain
connectivity. Consequently, no correlation has been estab
lished among the key parameters such as, synthesis,
processing, microstructure and electrical behavior of this
material; such correlation is inevitable in understanding the
underlying working mechanisms in electronic components
fabricated from them. For example, in the case of BTS
solid solutions [14], grains are interconnected and the
pores are channeled at the grain edges, giving a cylindrical
pore connection. Development of such a tailored micro
structure definitely requires intelligent processing with a
precise control over the processing parameters such as,
temperature, atmosphere, grain size, grain orientation,
length of grain boundaries, pore diameter, etc..

Thus, throughout the literature, there is a noticeable lack
of correlation of synthesis, processing and microstructural
aspects of the BaSnO$_3$ compound with its electrical
characteristics. Hence, it was relevant to initiate a study to
fill in this information gap on this material of technological
importance. The ceramic oxide was thoroughly studied
with respect to its synthesis, processing and characteriza
tion – physical, microstructural and electrical. A novel
preparative method such as the self-heat-sustained (SHS)
technique, in addition to the conventionally much-used
solid-state synthesis technique, was employed. Characteri
zation methods such as XRD and electron microscopy
(using scanning electron microscope with EDX) were used
to ascertain the reaction pathways leading to the formation
of the targeted compound, particle size and their dis
tribution and, to systematically follow the development of
microstructure in the sintered bodies. Similar investiga
tions on these aspects of CaSnO$_4$ and SrSnO$_3$ have
recently been reported [20,21]. In this paper, details of
synthesis, processing and microstructural evolution in the
BaSnO$_3$ system are presented. In a subsequent communic
ation, the results of the electrical measurements using the
a.c. immittance (impedance and/or admittance) spectro
scopic technique over a range of temperatures will be
reported and, a correlation among processing–microstruc
ture–electrical properties will be made [22].

2. Experimental

2.1. Materials synthesis and characterization

Metallic Sn (99.999% powder, Pi-Kem, Surrey, UK),
SnO$_2$ (99.995% powder, Aldrich, USA), and Ba(NO$_3$)$_2$
(99.5%, Hopkins and Williams, UK), were used as the
starting materials. Commercial grade nitric and hydrochlo
ric acids (16 M), liquid ammonia (14 M) and glacial acetic
acid, used as reagents and solvents in various syntheses
were procured from BDH, India, while isopropyl alcohol
(AR 95% minimum) was from James Burrough Ltd.,
(UK). Two different preparative techniques (solid-state and
self-heat-sustained) were employed for the synthesis of the
targeted compounds BaSnO$_3$ (Ba:Sn=1:1 molar). It
should be pointed out that the idea of adopting various
syntheses processes was two-fold: first, in the literature
available on this system, only the solid-state reaction route was adopted for sample preparation (see the details in the Section 2.2) and second, it was intended to find the most favorable synthesis technique in terms of the phase purity and benign microstructure in the sintered samples with most favorable electrical characteristics.

2.2. Solid-state reaction route

Stoichiometric amounts (1:1) of the compound Ba(NO₃)₂ crystals and SnO₂ powder of stated purity were weighed in a Mettler high precision electronic balance and dry mixed in an agate mortar. The mixture was then ball-milled for 4 h in isopropyl alcohol medium in airtight polystyrene bottles using clean zirconia balls as the milling medium. Room temperature drying under a UV lamp was used to remove isopropyl alcohol in a ventilated fume hood. Subsequently, the powder was pressed into discs 6 or 12 mm in diameter and 2–3 mm in thickness using stainless steel die at a pressure of about 100 MPa. The mixture was calcined first at 800°C for 8 h, crushed, repelletized and fired again at 1000°C for 24 h in air. The pellets were then pulverized and ground to a fine homogeneous powder which was subjected to phase analysis powder X-ray diffraction on a Scintag X-ray machine (USA) at room temperature, using monochromatic Cu Kα radiation (λ=1.5406 Å) in the range 10–90° (2θ). The resulting XRD pattern was also used to detect the presence of, if any, unreacted starting materials and/or new phases.

After the formation of “phase” pure compound was confirmed by XRD, the calcined powder was subjected to sintering (in order to follow the evolution of microstructure and its effect on the measured electrical properties) at three different temperatures, viz. at 1200, 1350 and 1600°C, for duration ranging from 2 to 72 h in ambient air. The sintering schedule adopted in this work is shown schematically in Fig. 1. In one case, however, the schedule was slightly modified and one sample from the batch of solid-state synthesis was sintered as follows:

RT–1350°C = 9 h; 1350–1600°C = 2.5 h
soaking @ 1600°C = 12 h; 1600°C–RT = 4 h.

Prior to sintering, the calcined powder was blended with 10 wt.% polyvinyl alcohol (PVA) as binder, dried under a UV lamp and pressed into green pellets by double-end compaction at pressure not exceeding 100 MPa. The use of polyfunctional organics such as polyvinyl alcohol or polyethylene glycol (PEG) is a common practice in the sintering of ceramic bodies, which plays an important role in the microstructural development; the organic binders are believed to provide strength and lubrication effect thereby bringing the particles in the green body closer to one another. This assists in achieving higher densities in sintered bodies than those sintered without the binder. The choice of PVA in this work was due to its relatively easier combustion kinetics compared to those of PEG. Microstructural features of the starting “green” BaSnO₃ powder as well as the sintered discs were determined by using a JEOL-6400SM scanning electron microscope (Japan). Elemental identification and quantification in different regions of the sintered samples were carried out by using the EDX analyzer (Link eXL, UK) attached to the above SEM machine (Table 1). Owing to the strong susceptibility of compounds in the Ba–Sn–O systems towards moisture, the calcined powder as well as the sintered discs were always stored in a humidity-free desiccator containing anhydrous CaCl₂, unless required for microscopic/electrical measurements.

2.3. Self-heat-sustained (SHS) route

Metallic tin powder was intimately mixed with anhydrous Ba(NO₃)₂ crystals in a 1:1 molar ratio. The mixture was placed in a platinum boat and first heated slowly to and maintained at 250°C for 4 h so as to facilitate complete melting of metallic tin (m.p. = 232°C) and its uniform dispersion under gravitational flow in the liquid state. The temperature was then raised gradually to 800°C and maintained for another 4 h to cause the reaction between molten and free flowing tin and Ba(NO₃)₂. The mixture was next calcined at 1100°C for 12 h. XRD analysis of the

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resulting powder at this stage revealed the presence of a two-phase (Ba,SnO$_4$ + BaSnO$_3$) mixture. This necessitated further heating of the mixture at 1200°C for 24 h. Phase identification was carried out by X-ray as mentioned in the above subsection, both after 1100 and 1200°C calcination steps, the reason for which will be discussed in Section 3. A schematic of the experimental setup for the synthesis of BaSnO$_3$ via SHS technique has been shown and described elsewhere [20]. The mass thus obtained was crushed, pulverized, mixed with PVA and sintered according to the (T–t) schedule adopted in the case of the solid-state derived sample. The details of microscopic examination of the SHS derived sample remain identical to those described above.

3. Results and discussion

3.1. Solid-state reaction route

Fig. 2(a) shows the X-ray diffraction pattern of the sample prepared by solid-state reaction between Ba(NO$_3$)$_2$ and SnO$_2$, which matches with the standard reported (JCPDS card No. 15-0780), indicating the formation of the intended compound, viz. BaSnO$_3$ in a single phase. The appearance of very sharp diffraction peaks further indicates quite small crystallite size in the powder. The absence of diffraction peaks due either to the starting materials or second phases in the Ba–Sn–O system, showed the powder obtained, to be of high quality. The formation of BaSnO$_3$ via solid-state reaction takes place as follows:

$$2\text{SnO}_2(s) + 2\text{Ba(NO}_3)_2 \rightarrow 2\text{BaSnO}_3(s) + 4\text{NO}_2(g) + \text{O}_2(g).$$

(1)

It should be noted that, while the sample preparation via solid-state route was done by following the conventional route, the compound formation according to Eq. (1) occurred at relatively lower calcination temperature (1000°C/24 h). This is rather encouraging in the case of the solid-state technique where usually larger grains are formed due to the use of high temperature and several repetitions of the “heat and beat” steps. We attribute this improvement in the present case to the use of metal nitrate as one of the precursors rather than the conventionally employed carbonate or oxide; the metal nitrates have more favorable decomposition kinetics compared to their carbonate counterparts. This is a definite improvement over the procedure of compound formation reported by Smith et al. and Upadhyay et al. [16,19]. While Smith et al. reported the synthesis of BaSnO$_3$ by heating stoichiometric amounts of BaCO$_3$ and SnO$_2$ at 1200°C for 16 h, calcination at 1200°C/6 h and “repeated grinding, pelleting and firing several times” has been reported by Upadhyay et al. [19]. Moreover, it is not clear from the latter report whether the cycle of grinding, pelleting and firing was repeated with the calcined powder or the sintered material.

The microstructural features of the solid-state derived samples sintered at 1200°C as a function of soak time between 24 to 72 h is shown in Fig. 3(a–e). From these SEM micrographs, it can be seen that sintering at 1200°C for 24 h led to a microstructure with abnormal initial grain growth, having a broad grain size distribution, ranging from submicron to as large as ~6 μm in some pockets. This evidently left a significant amount of porosity in the sample. As the soak time was increased to 48, 60 and 72 h, very shapely and characteristic “sugar cube” type grains with 3–7 μm in edge dimension evolved (Fig. 3(b–d)) with a clearly visible narrowing of the grain size distribution. Taking into account that BaSnO$_3$ crystallizes in cubic perovskite structure having a cell constant of 4.119 Å, it appears that the grains, on average, had grown to an extent of about 10 000 times the unit cell dimension. This is about 200 times that reported by Uphadhyay et al. [19] in their sample sintered at 1400°C for 6 h. It can also be seen from Fig. 4(a–d), that even with such phenomenal grain growth and preferred grain orientation, a significant amount of porosity was left in the material. The mechanism of formation of such large grains seemed to follow the sequence shown in Fig. 3(e) (microstructure of a sample sintered at 1200°C for 72 h at higher magnification). Smaller grains (on the top), cubic in shape and ~1 μm in size, seem to join together and grow into larger ones, as seen in the background.

In order to cause sufficient grain-to-grain connectivity and reduced porosity, sintering at 1600°C for 2 and 12 h was resorted to, and the resulting microstructure is shown in Fig. 4. The microstructures marked a and b are for samples sintered for 2 h, at two different magnifications (×500 and ×2000, respectively), while c and d are for those sintered at 1600°C for 12 h at the same magnification. At lower magnification (Fig. 5(a,c)), almost monosized grains (~3–4 μm, estimated from higher magnification micrographs) can be seen for both 2 and 12 h sintering at 1600°C. Fig. 4(c,d), however, clearly show that the sample is still porous and exhibits “sugar cube” features, with edges rather smoothened. Nevertheless, the grain-to-grain connectivity in these samples appeared to have improved. Density measurements on the sintered bodies, by making use of the pellet dimensions and mass, revealed that the relative density was only up to 70–80% of theoretical value even in samples sintered at 1600°C for 12 h; this fact is corroborated very well by the microstructural features discussed above.

In the light of the foregoing discussion, it appears that in the solid-state derived BaSnO$_3$ samples, a high degree of densification cannot be achieved in the temperature range used for sintering in this study. It is envisaged, however, that soaking at 1600°C for a duration longer than 12 h might result in a microstructure with improved intergranular connectivity and reduced porosity.
Fig. 2. Powder X-ray diffraction patterns of BaSnO$_3$ samples synthesized via (a) the solid-state reaction route and (b) the SHS technique. XRD signature in (b) consists of a mixture of those due to Ba$_2$SnO$_4$ and BaSnO$_3$.

At this juncture, it is worth comparing the sintering behavior of BaSnO$_3$ with that of CaSnO$_3$ and SrSnO$_3$, obtained via a similar solid-state route [20,21], in order to follow the systematic, if any, among the three stannates. In the case of CaSnO$_3$, it was observed that a highly dense microstructure with near zero porosity and uniform grain size (without much growth) could be developed by sintering at 1200°C for up to 48 h. Sintering at 1350°C led to nonuniform grain growth in addition to somewhat increased porosity. In the case of SrSnO$_3$, sintering at 1200°C was found to be inadequate even up to 72 h soaking, as evidenced by the presence of cubic agglomerates, consisting of 20–30 grains of varying size lumped together. Microstructures with 10–15% porosity and uniform grain size (~1 μm) could be developed by sintering SrSnO$_3$ at 1350°C up to 24 h. Sintering at 1600°C even for a short time (2 h) was found to be too severe, as it led to increased but well-connected porosity, without causing any significant grain growth. All along, very small grain size of the order of 1 μm or less, was a very characteristic feature
of solid-state derived SrSnO₃ samples. In comparison to these, the present work showed that sintering of BaSnO₃ proved to be the most difficult. Sintering even up to 1600°C for 12 h could not eliminate porosity in order to yield a typically dense ceramic structure.

3.2. Self-heat-sustained (SHS) reaction route

The self-propagating high-temperature or self-heat-sustained (SHS) synthesis is an attractive and viable alternative to the conventional methods of advanced materials production, which is gaining rapid popularity in the field of ceramic- and metal-matrix composites (CMC and MMC) [23]. The most attractive feature of the SHS technique is the ability of highly exothermic reactions to be self-sustained and therefore, energetically efficient. The rationale behind using metallic tin in the present case, was its rather low temperature of melting (⟨Sn⟩= 232°C; ΔHₘ = 7.056 kJ g atom⁻¹) [24], affecting a homogeneous mixing and reactivity with the metal nitrate, yielding a
Fig. 4. Microstructure of solid-state derived BaSnO₃ sintered at 1600°C for: (a±b) 2 h and (c±d) for 12 h; magnification is ×500 (a, c) and ×2000 (b, d).

“phase” pure compound under less demanding conditions than those reported hitherto.

Fig. 3(b) shows the X-ray diffraction pattern of the BaSnO₃ sample obtained by the SHS technique after 1100°C/12 h. In this case, the compound formation was found to have initiated at about 800°C. The XRD signature of the sample after the 1100°C calcination step (Fig. 3(b)), however, shows a mixture of peaks corresponding to a Ba-rich phase, viz. Ba₂SnO₄ (JCPDS card No. 12-0665), in addition to those belonging to the intended compound BaSnO₃. Nevertheless, the XRD pattern of the sample calcined further at 1200°C conformed to that reported for pure BaSnO₃ and was identical to that obtained on the solid-state derived one. For the sake of obviating repetition, the XRD pattern of the later sample has not been shown. The scheme of BaSnO₃ formation in this case, therefore, seems to be via an intermediate Ba-rich phase, Ba₂SnO₄. It is likely that in the initial stages, molten metallic tin reacted in the following way:

\[
\text{Sn(l) + 2Ba(NO}_3\text{)}_2 \rightarrow \text{Ba}_2\text{SnO}_4 + 4\text{NO}_2(g) \uparrow \\
\text{Sn(l) + Ba(NO}_3\text{)}_2 + \frac{1}{2}\text{O}_2(g) \rightarrow \text{BaSnO}_3 + 2\text{NO}_2(g) \uparrow.
\]

The Ba-rich phase subsequently reacted with more Sn or SnO₂ to form BaSnO₃ as shown below:

\[
\text{Ba}_2\text{SnO}_4 + \text{Sn(l)} + \text{O}_2(g) \rightarrow 2\text{BaSnO}_3
\]

\[\text{[or] } \text{Ba}_2\text{SnO}_4 + \text{SnO}_2(s) \rightarrow 2\text{BaSnO}_3.\]

This reaction scheme is corroborated by the XRD signature of the 1:1 molar mixture of metal nitrate and tin, obtained on samples heated at 800°C/8 h +1100°C/12 h and at 1200°C/24 h, respectively. Evolution of heat due to the fusion of tin at rather low temperature is believed to have aided the above scheme of the reaction pathway. Moreover, this reaction sequence is identical to those observed in the formation of Ca- and Sr-stannate via the SHS technique [20,21]. This is the first report in the literature where a technique other than the solid-state method for the synthesis of BaSnO₃ has been adopted. As mentioned in Section 3.1, the preparative details reported by other workers on this and analogous systems (Ca- and Sr-stannate) are rather incomplete and obscure. For example, Mandal et al. [25] Parkash et al. [26] and Upadhyay et al. [19] have reported the solid-state synthesis of Ca-, Sr- and BaSnO₃, respectively, by mixing respective metal carbonates and tin dioxide in acetone medium, calcining at 1200°C/4 h (6 h in the case of BaSnO₃) and, sintering at 1350°C for 12 h (in the case of BaSnO₃, first at 1250°C for 6 h followed by 12 h at 1350, 1375 and 1400°C each), repeating the process “several” times. Shimizu et al. [7]
used an identical technique for making doped-SrSnO$_3$, ball milling the SrCO$_3$ and SnO$_2$ mixture overnight, calcining at 1000°C for 2 h and, finally sintering at 1100–1200°C for “several” hours. Similarly, Smith et al. [16] synthesized the compound by heating the carbonate–oxide mixture at 1200°C for 16 h and annealing at 1300°C for 43 h, while Bao et al. [18] used sintering at 1000°C only. As discussed in Section 3.1, solid-state derived BaSnO$_3$ samples could only be sintered partially, even after soaking for 12 h at 1600°C.

Fig. 5 shows the morphology of the raw powder derived via the SHS route; Fig. 5(a) is the SEM picture of the powder after the 1100°C/12 h calcination step, while Fig. 5(b) is taken of the powder after the 1200°C/24 h. While Fig. 5(a) revealed that the raw powder was submicron in size, mostly in the form of agglomerates, the morphology seemed to have undergone significant change after 1200°C calcination, in terms of homogeneity of the powder and shape and size of the grains. This microstructural feature is evidence that the formation of BaSnO$_3$ in the case of the self-heat-sustained reaction might have proceeded by the steps shown by reactions (2–5) above.

In the case of the SHS derived BaSnO$_3$, sintering began at 1350°C and the microstructure resulting after sintering for 24 and 36 h is shown in Fig. 6. As can be clearly seen, the microstructural features (“sugar cube” grains) in this case are almost identical to those observed in the case of solid-state derived samples, albeit with much larger distribution of the particle size; in this case, the average size ranged from 1 to about 20 μm in some overly grown grains. While going from 24 to 36 h soak-time (Fig. 6(a,b) respectively), there was a noticeable reduction in porosity, the broad grain size distribution, nevertheless, still remaining. Measurements on SHS derived samples sintered at 1350°C for 36 h showed improved density (~78% theoretical). It is well-known, however, that one of the major limitations of SHS synthesis is the presence of a relatively higher degree of porosity in the final product. Nevertheless, since about 95% of this porosity is “open” in nature, it can be eliminated during the sintering step, thereby leaving a dense and compact body. In can be suggested therefore, that a longer firing at 1350°C, might result in a further reduction in porosity, but whether the nonuniformity of the grain size could also be eliminated, is questionable and needs more experiments.

For reasons mentioned in Section 3.1 with respect to sufficient grain-to-grain connectivity with reduced porosity and uniform particle size, sintering at 1600°C was resorted to, and the resulting microstructure is shown in Fig. 7. The
Fig. 7. Microstructural development in SHS derived: (a) BaSnO$_3$ samples sintered at 1600°C for 2 h, (b) CaSnO$_3$ samples sintered at 1600°C for 2 h, (c) SrSnO$_3$ samples sintered at 1350°C for 12 h and, (d) SrSnO$_3$ samples sintered at 1600°C for 2 h.

Drastic morphological and structural changes subsequent to firing at 1600°C for 2 h, can be compared to those sintered at lower temperatures and also with those of samples derived from solid-state technique (Figs. 3 and 4). The resulting features included: highly densified material with near zero porosity, proper grain orientation and, good intergranular connectivity. The “sugar cube” features have been replaced by the spherical grains which are common in ceramic microstructures (average size 1–2 μm). This also resulted in a significant improvement in the density of the sintered body.

Comparison of the evolution of microstructure in BaSnO$_3$ samples obtained by the self-heat-sustained reaction technique with that in CaSnO$_3$ and SrSnO$_3$ from the same synthesis route, brings out the following observations:

1. A well-densified microstructure with small grain size (~1 μm) and zero or near zero porosity can be obtained by choosing a sintering schedule of 1350°C/x h (48 h<x≤48 h) for CaSnO$_3$ samples. Very well sintered samples with relatively larger grains (3–5 μm) and minimal porosity could also be obtained by sintering at 1600°C for 2 h (Fig. 7(b)); sintering for longer duration at this temperature, however, led to abnormal grain growth and severe morphological variation [20].

2. In SrSnO$_3$ samples, well-densified microstructure with small grain size and zero or near zero porosity can be obtained by choosing a sintering schedule of 1350°C/x h (12 h<x≤24 h) (Fig. 7(c)). However, the microstructure changed drastically in SrSnO$_3$ sintered at 1600°C for 2 h, resulting in highly oriented hexagonal-shaped 3-D grains, 3–5 μm in size (Fig. 7(d)).

That there was no materials degradation in terms of compositional variation and formation of new phases rich in either Sn or Ba, as a result of sintering at temperatures in the range 1200–1600°C, was confirmed by performing elemental analyses and quantification of segregation by energy dispersive X-ray (EDX) analyses. The EDX analyses (in terms of concentration profiles of Ba and Sn) were performed in different regions of each of the sintered samples and some typical results are shown in Fig. 8. Such an exercise showed the ratio of Ba:Sn to be 1:1 in all the
samples. Thus, there was no degradation of material, nor was there noticed any loss of material due to preferential evaporation of the sample.

4. Conclusions

The compound BaSnO$_3$ has been investigated in much detail with respect to its synthesis by different routes, processing under different sintering conditions and examining the resulting microstructural features. Two different methods of material synthesis, viz. conventional solid-state and the novel self-heat-reaction (SHS) techniques were employed and reaction pathways leading to the compound formation were closely followed. X-Ray diffraction and electron microscopic techniques were extensively used to understand the evolution of phases and microstructures as a result of sintering cycles. On the basis of this, the following conclusions could be drawn:

1. Synthesis by the modified solid-state route using nitrate (instead of carbonate) precursor helped the calcination and compound formation temperature to be lowered by a significant 200 degrees margin. Microstructure con-
taining characteristic “sugar cube” shaped grains with 3–7 μm in edge dimension evolved with sintering at 1200°C up to 72 h; even with such phenomenal grain growth and preferred grain orientation, significant amount of porosity was left in the material. Sintering even up to 1600°C for 12 h could not eliminate porosity in order to yield a typically dense ceramic structure. Thus, solid-state synthesis does not appear to be an attractive route for BaSnO as long as the microstructural features are concerned (in the temperature-time range employed for sintering in the present investigation). However, in this case, liquid phase sintering could be attempted, using low melting compounds such as Bi₂O₃ (T_m = 825°C) and/or V₂O₅ (T_m = 670°C). In such cases, the driving force for densification is provided by the capillary pressure of the liquid phase located between the fine solid particles [27]. Such a treatment might lower the temperature of sintering as well.

2. As in the case of CaSnO₃ and SrSnO₃ synthesized via the SHS technique [20,21], compound formation seems to have initiated at temperatures as low as 800°C in the case of BaSnO₃; the formation of BaSnO₃ was complete at 1200°C and appeared to be facilitated via a two-stage process involving the formation of an intermediate Ba-rich phase, Ba₂SnO₅, as evidenced by XRD. Small grain size and a narrower particle size distribution was an interesting feature of the SHS derived raw powder. Sintering at 1350°C for soak-time in the range 24–36 h was found to yield microstructural features almost identical to those observed in the case of solid-state derived samples (“sugar cube” grains). In this case, the average size ranged from 1 to about 20 μm in some overly grown grains. The SHS derived BaSnO₃ samples could be densified to the desired level by sintering the powder compacts at 1600°C for 2 h, with benign microstructural features, typical of ceramics.

3. A comparison of microstructural evolution in BaSnO₃, with that in CaSnO₃ and SrSnO₃ shows a systematic trend in the gradual transition of sintering condition, as one goes from calcium to strontium to barium stannate. This trend can be explained in terms of increasing ionic size (from 99 pm for Ca²⁺ to 112 pm for Sr²⁺, to 134 pm for Ba²⁺). This difference in ionic size affects the solid-state diffusion kinetics in the corresponding ceramic – an important criterion for sintering via diffusion. A smaller ion such as Ca²⁺ can diffuse faster than Ba²⁺. Hence, the sintering in CaSnO₃ is favored and accomplished at relatively lower temperature (1200°C up to 48 h). The opposite is the case with BaSnO₃, where a relatively high temperature (1600°C) is effective to result in well-densified, pore-free microstructure, where the starting material is obtained via the SHS technique. In addition, these stannates are line compounds with no nonstoichiometry either with respect to metal or oxygen. This is an important factor, which otherwise contributes to the sintering via cationic or anionic defect formation. Such behavior has been well documented in the case of solid-state sintering of barium titanate ceramics [2–4].

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