

Low temperature synthesis of $\text{Ba}_{1-x}\text{Sr}_x\text{SnO}_3$ ($x = 0-1$) from molten alkali hydroxide flux

B RAMDAS and R VIJAYARAGHAVAN*

Materials Division, School of Advanced Sciences, VIT University, Vellore 632 014, India

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Abstract. Perovskite structured stannates ($\text{Ba}_{1-x}\text{Sr}_x\text{SnO}_3$, $x = 0.0-1.0$) powders have been synthesized for the first time by molten salt synthesis (MSS) method using KOH as the flux at lower temperature (400°C) compared to other methods. The phase formation was confirmed by FT-IR spectroscopy, powder X-ray diffraction (XRD) and the microstructure was analysed by scanning electron microscopy. XRD patterns reveal the formation of single phasic products for parent and substituted products with good crystallinity throughout the range ($x = 0.0-1.0$). The morphology of the particles of BaSnO_3 and SrSnO_3 is spherical and rod shaped, respectively. Effect of soaking periods on the grain growth is observed clearly in SrSnO_3 . $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{SnO}_3$ (BSS5) crystallizes in flake like morphology.

Keywords. Perovskite; stannates; molten salt synthesis; X-ray diffraction; scanning electron microscopy.

1. Introduction

Alkaline earth stannates, ASnO_3 ($A = \text{Ba}, \text{Sr}, \text{Ca}$) with perovskite structure, are of great industrial and technological interests due to their attractive dielectric characteristics finding different applications (Jaffe *et al* 1971; Subbarao 1981). For example, BaSnO_3 – BaTiO_3 solid solution is used to fabricate ceramic boundary layer capacitors (Wernicke 1978). BaSnO_3 has also been investigated as a promising sensor material for the detection of host gases such as CO , Cl_2 , reducing gases ($\text{C}_2\text{H}_5\text{OH}$, NO_x , LPG and CH_3SH) and humidity (Shimizu *et al* 1989; Moseley *et al* 1991; Lampe *et al* 1995a, b; Gopal Reddy *et al* 2001). Recently, it is also proved to have photocatalytic activity (Zhang *et al* 2007).

In order to modify suitably the properties of ASnO_3 ($A = \text{Ba}, \text{Sr}$) many substitutions have been carried out at A and Sn sites (Trari *et al* 1994; Parkash *et al* 1996; Thangadurai *et al* 2002; Bajpai *et al* 2003; Kumar *et al* 2005; Upadhyay *et al* 2007). Kumar *et al* (2006) studied the effect of microstructure on the properties of Sr substituted BaSnO_3 synthesized ceramic method.

Various methods have been employed to prepare the pure and substituted perovskite structured stannates. Commonly, BaSnO_3 is prepared by solid state reaction between BaCO_3 and SnO_2 at elevated temperature of $1000-1200^\circ\text{C}$. It frequently leads to relatively larger grain size and formation of intermediate phase of

Ba_2SnO_4 during synthesis along with SnO_2 impurity (Wagner and Binder 1958). Hence, low temperature chemical methods have been adopted by many researchers. Although BaSnO_3 has been synthesized at low temperature by precipitation method, the product is invariably contaminated with impurities of SnO_2 and BaCO_3 (Coffeen 1953; Tao *et al* 2000). Peroxide method involving peroxo precursor requires high calcination temperature of 1000°C (Pfaff 1993). Presence of carbonates has been reported even at a calcination temperature of 1000°C during the synthesis of SrSnO_3 and BaSnO_3 by polymeric complex method (Udawatte *et al* 2000). In hydrothermal synthesis of these stannates (Buscaglia *et al* 2003; Lu and Schmidt 2005) at low temperature, the product contains OH^- ions in lattice even at a calcination temperature of 1200°C .

We have attempted to synthesize pure and solid solution, $\text{Ba}_{1-x}\text{Sr}_x\text{SnO}_3$, by molten salt synthesis method with an objective to obtain well-crystalline perovskite stannates at lower temperature. Good crystallinity is important for photocatalytic activity (Zhang *et al* 2007) which can be achieved by MSS at low temperature compared to other methods. MSS method is a well established low temperature synthetic method that has attracted increasing interest recently. It is a non-topochemical route that has enabled the synthesis of many oxides belonging to perovskite, pyrochlore and K_2NiF_4 structured oxides (Uma and Gopalakrishnan 1993; Gopalan *et al* 1996; Shiva Kumara *et al* 2003). To the best of our knowledge, synthesis of MSnO_3 ($M = \text{Ba}, \text{Sr}$) and its solid solution by molten salt synthetic method has not yet been reported.

*Author for correspondence (rvijayaraghavan@vit.ac.in)

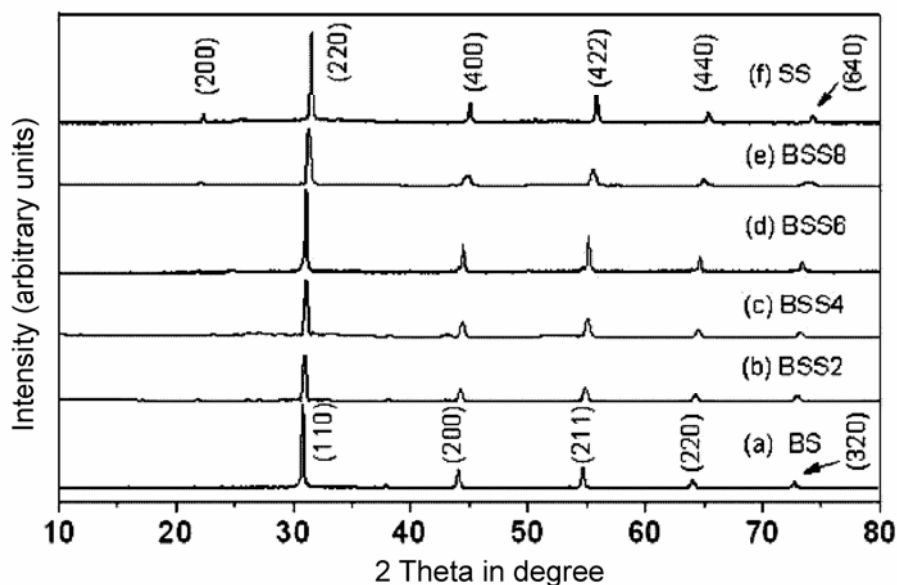


Figure 1. Powder-XRD patterns of $\text{Ba}_{1-x}\text{Sr}_x\text{SnO}_3$ ($x = 0.0, 0.2, 0.4, 0.6, 0.8$ and 1.0) synthesized using KOH flux at 400°C for 6 h.

2. Experimental

$\text{Ba}_{1-x}\text{Sr}_x\text{SnO}_3$ ($x = 0-1$) phases were synthesized by MSS using KOH alkali flux as follows. All the chemical reagents used were of analytical grade. $\text{Ba}(\text{OH})_2 \cdot 8\text{H}_2\text{O}$ (99% powder, Thomas Baker, India), SnO_2 (99.5% powder, Thomas Baker, India), $\text{Sr}(\text{NO}_3)_2$ (99% powder, Thomas Baker, India) were used as the starting materials. Stoichiometric ratios of these salts were mixed in an agate mortar and pestle. This mixture was added to alkalis, KOH and NaOH of 30 g in recrystallized alumina crucible. The resultant mixture was then heated at 400°C for 6, 12 and 24 h in a furnace and allowed to furnace cool. The product was finally washed several times with distilled water to remove the alkali and dried at 120°C for 6 h. SrSnO_3 and the solid solutions were also prepared in a similar way. The products were characterized by powder X-ray diffraction (PAN analytical X'Pert Pro) with $\text{CuK}\alpha$ radiation, FT-IR (Thermo Nicolet, Avatar 330 FTIR Spectrometer, USA), scanning electron microscopy (SEM) (HITACHI Model S-3000H) and flame photometry.

3. Results and discussion

3.1 IR spectroscopy

FT-IR spectra of the products conform to the reported data (Nyquist and Kagil 1971; Azad *et al* 2000) with the bands around 650 cm^{-1} corresponding to Sn-O frequency of SnO_6 octahedra.

Table 1. Lattice parameter of $\text{Ba}_{1-x}\text{Sr}_x\text{SnO}_3$.

Code	Composition	Cubic unit cell parameter (Å)	Volume (Å ³)
BS	BaSnO_3	4.110(3)	69.4
BSS2	$\text{Ba}_{0.8}\text{Sr}_{0.2}\text{SnO}_3$	4.101(5)	69.0
BSS4	$\text{Ba}_{0.6}\text{Sr}_{0.4}\text{SnO}_3$	4.085(6)	68.2
BSS6	$\text{Ba}_{0.4}\text{Sr}_{0.6}\text{SnO}_3$	4.078(7)	67.9
BSS8	$\text{Ba}_{0.2}\text{Sr}_{0.8}\text{SnO}_3$	4.060(8)	67.0
SS	SrSnO_3	4.043(0)	66.1

3.2 X-ray diffraction

XRD patterns of the phases of BaSnO_3 (BS), SrSnO_3 (SS) and its solid solution, $\text{Ba}_{1-x}\text{Sr}_x\text{SnO}_3$ ($x = 0.2, 0.4, 0.6$ and 0.8 coded as BSS2, BSS4, BSS6 and BSS8), obtained by MSS method at 400°C for 6h are shown in figure 1. XRD patterns of BaSnO_3 (figure 1a) and SrSnO_3 (figure 1f) reveal the formation of single phasic cubic and pseudocubic structure, respectively. XRD patterns (figures 1b-e) of the solid solutions are also single phasic and crystalline. All the diffraction peaks of the solid solution are shifted towards higher diffraction angles due to the substitution of smaller Sr^{2+} (1.44 Å) in place of bigger Ba^{2+} (1.61 Å) site (Shannon 1976).

All these substituted phases could be indexed in cubic/pseudocubic structure. The lattice constants by least square refinement are given in table 1. The variation of lattice constants with the composition is found to obey Vegard's law. The parameters are also consistent with the

literature reported values (Udawatte *et al* 2000). Although $SrSnO_3$ could be refined as a pseudocubic unit cell, high resolution X-ray diffraction indicates that it crystallizes in orthorhombic structure (Zhang *et al* 2007).

Both $BaSnO_3$ and $SrSnO_3$ are formed only in KOH flux but not in NaOH flux. It may be due to the stronger oxidizing power of KOH than NaOH. Hence, the formation of super-oxide is more favourable in KOH than in NaOH (Shiva Kumara *et al* 2003) which is a crucial factor in MSS. The solid solutions are not formed even in the eutectic flux ratio of KOH and NaOH, but formed only in KOH flux. We also tried to synthesize Ba_2SnO_4

using KOH flux but have ended up with perovskite phase only.

3.3 Microstructure analysis

Figure 2 shows the SEM micrograph of $BaSnO_3$ powders prepared using KOH flux at 400°C with soaking duration of 6, 12 and 24 h. $BaSnO_3$ soaked for 6 h (figure 2a) shows agglomeration of uniform particles in the sub-micron range. No significant microstructural changes were observed with increasing soaking periods (figures 2b and c). Figure 3 shows the micrographs of $SrSnO_3$ powders prepared using KOH flux with soaking durations

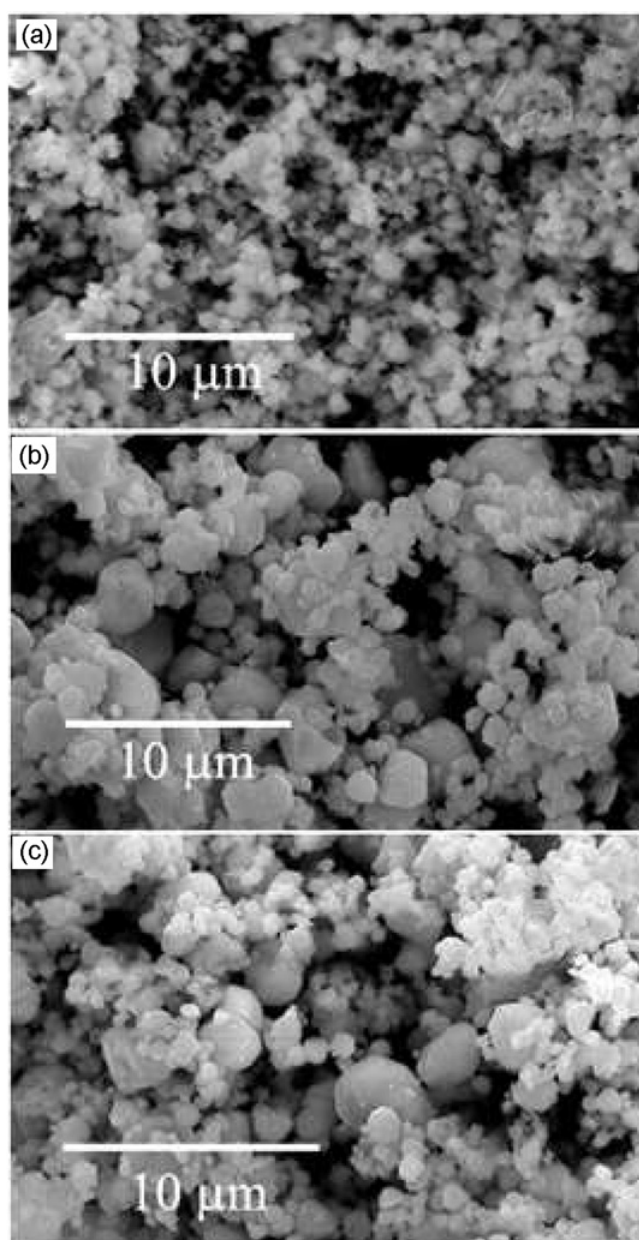


Figure 2. SEM micrographs of $BaSnO_3$ synthesized using KOH flux at 400°C with different soaking durations: (a) 6 h, (b) 12 h and (c) 24 h.

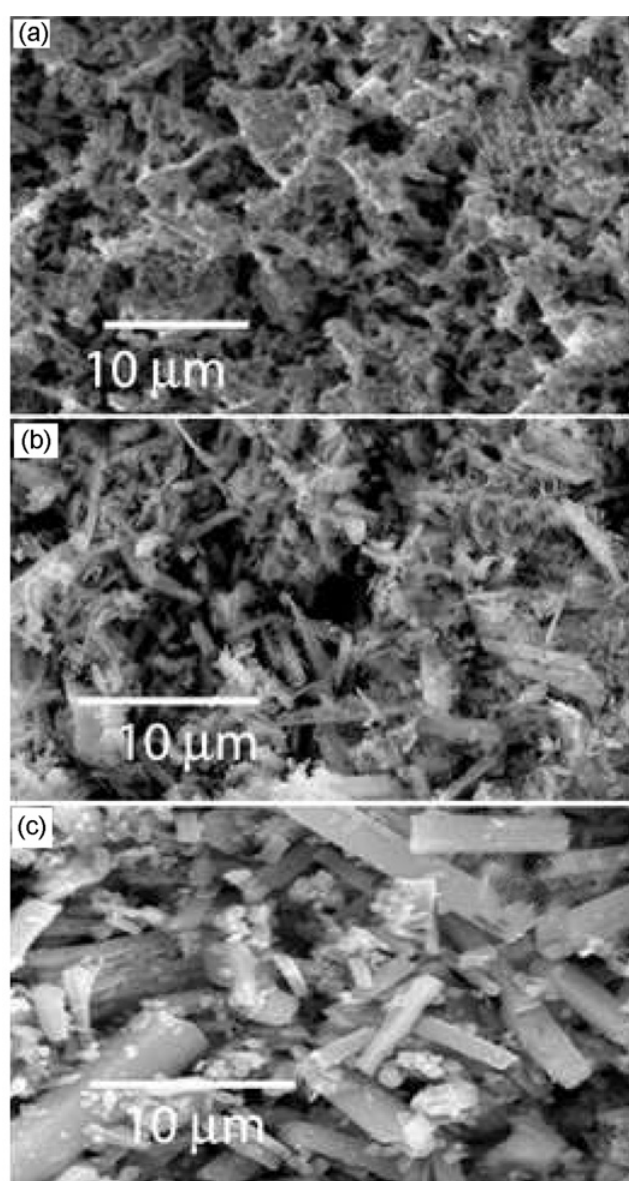


Figure 3. SEM micrographs of $SrSnO_3$ synthesized using KOH flux at 400°C with different soaking durations: (a) 6 h, (b) 12 h and (c) 24 h.

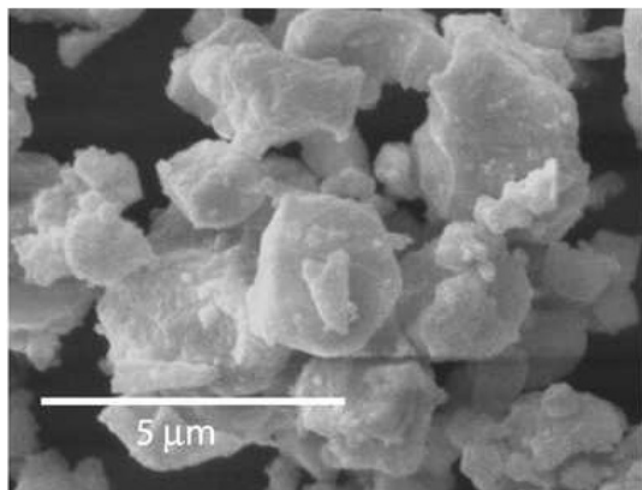


Figure 4. SEM micrograph of BSS5 synthesized using KOH flux at 400°C for 24 h.

of 6, 12 and 24 h. Figure 3a shows the fibrous structure of the crystallites obtained for a soaking period of 6 h. These fibres are almost agglomerated forming a bundle shape along with small aggregated particles. On increasing the soaking period from 6 to 24 h, the grain growth was found to occur as shown in figures 3a–c, which clearly reveal the growth of the fibrous bundles to rod-shape structure. The rods are of length 5–10 μm. SEM micrograph of $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{SnO}_3$ (BSS5) shown in figure 4 indicates the morphology to be flake like. The particles sizes are in the range of 2–5 μm.

The composition of the parent phases was checked by energy dispersive X-ray analysis (EDX) in spot mode. The EDX results showed that the metal ions are in 1 : 1 ratio, showing uniform stoichiometry of the compounds.

3.4 Flame photometry

Flame photometry showed that there is no detectable potassium incorporation into the stannates prepared by alkali (KOH) flux method.

4. Conclusions

Single phasic perovskite stannates ($\text{Ba}_{1-x}\text{Sr}_x\text{SnO}_3$, $x = 0.0\text{--}1.0$) have been synthesized employing molten KOH as flux at a temperature as low as 400°C. Morphology of SrSnO_3 is affected by soaking duration while BaSnO_3 shows no significant grain growth with soaking duration. Solid solution stannate (BSS5) crystallizes in flake shapes. These stannates can only be synthesized in KOH flux but not in NaOH flux.

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References

- Azad A M, Hashim M and Baptist S 2000 *J. Mater. Sci.* **35** 5475
 Bajpai P K, Ratre K, Pastor M and Sinha T P 2003 *Bull. Mater. Sci.* **26** 461
 Buscaglia M T, Leoni M, Viviani M and Buscaglia V 2003 *J. Mater. Res.* **18** 560
 Coffeen W W 1953 *J. Am. Ceram. Soc.* **36** 207
 Gopal Reddy C V, Manorama S V and Rao V J 2001 *J. Mater. Sci.: Mater. Electron.* **12** 137
 Gopalan S, Mehta K and Vikar A V 1996 *J. Mater. Res.* **11** 1863
 Jaffe B, Cook W R and Jaffe H 1971 *Piezoelectric ceramics* (New York/London: Academic Press) Ch. 5 and 12
 Kumar A, Singh B P, Choudhary R N P and Thakur A K 2005 *Mater. Lett.* **59** 1880
 Kumar A, Singh B P, Choudhary R N P and Thakur A K 2006 *Ceram. Int.* **32** 73
 Lampe U, Gerblinger J and Meixner H 1995a *Sens. Actuators B24–25* 657
 Lampe U, Gerblinger J and Meixner H 1995b *Sens. Actuators B26–27* 97
 Lu W and Schmidt H 2005 *J. Euro. Ceram. Soc.* **25** 919
 Moseley P T, Stoneham A M and Williams D E 1991 *Techniques and mechanisms in gas sensing* (Bristol: Adam Hilger) Ch. 4
 Nyquist R A and Kagil R D 1971 *Infrared spectra of inorganic compounds* (New York: Academic Press) pp 108, 128
 Parkash O, Mandal K D, Christopher C C, Sastry M S and Kumar D 1996 *J. Mater. Sci.* **31** 4705
 Pfaff G 1993 *J. Euro. Ceram. Soc.* **12** 159
 Shannon R D 1976 *Acta Crystallogr.* **A32** 751
 Shimizu Y, Shimabukuro M, Arai H and Seiyama T 1989 *J. Electrochem. Soc.* **136** 1206
 Shiva Kumara C, Hedge M S, Prakash A S, Khadar A M A, Subbanna G N and Lalla N P 2003 *Solid State Sci.* **5** 351
 Subbarao E C 1981 *Ferroelectric* **35** 143
 Tao S, Gao F, Liu X and Sorensen O T 2000 *Sens. Actuators B71* 223
 Thangadurai V, Schmid-Beurmann P and Weppner W 2002 *Mater. Res. Bull.* **37** 599
 Trari M, Doumerc J P, Dordor P P, Pouchard M, Behr G and Krabbes G 1994 *J. Phys. Chem. Solids* **55** 1239
 Udawatte C P, Kakihana M and Yoshimura M 2000 *Solid State Ionics* **128** 217
 Uma S and Gopalakrishnan J 1993 *J. Solid State Chem.* **105** 595
 Upadhyay S, Parkash O and Kumar D 2007 *J. Electroceram.* **18** 45
 Wagner G and Binder H 1958 *Z. Anorg. Allg. Chem.* **297** 328
 Wernicke R 1978 *Ber. Deut. Keram. Ges.* **55** 356
 Zhang W, Tang J and Ye J 2007 *J. Mater. Res.* **22** 1859