Low temperature synthesis of $Ba_{1-x}Sr_xSnO_3$ ($x = 0$–1) from molten alkali hydroxide flux

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Abstract. Perovskite structured stannates ($Ba_{1-x}Sr_xSnO_3$, $x = 0\cdot0$–$1\cdot0$) 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 ($x = 0\cdot0$–$1\cdot0$). 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 $SrSnO_3$. $Ba_{0\cdot5}Sr_{0\cdot5}SnO_3$ (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 = Ba, Sr, Ca) with perovskite structure, are of great industrial and techno-logical interests due to their attractive dielectric charac-teristics 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 inve-stigated as a promising sensor material for the detection of host gases such as CO, Cl_2, reducing gases (C_2H_5OH, 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 = Ba, 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 sub-stituted $BaSnO_3$ 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°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 research-ers. 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 carbo-nates 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 solu-tion, $Ba_{1-x}Sr_xSnO_3$, by molten salt synthesis method with an objective to obtain well-crystalline perovskite stan-nates at lower temperature. Good crystallinity is impor-tant 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 increas-ing 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 = Ba, Sr) and its solid solution by molten salt synthetic method has not yet been repor-ted.

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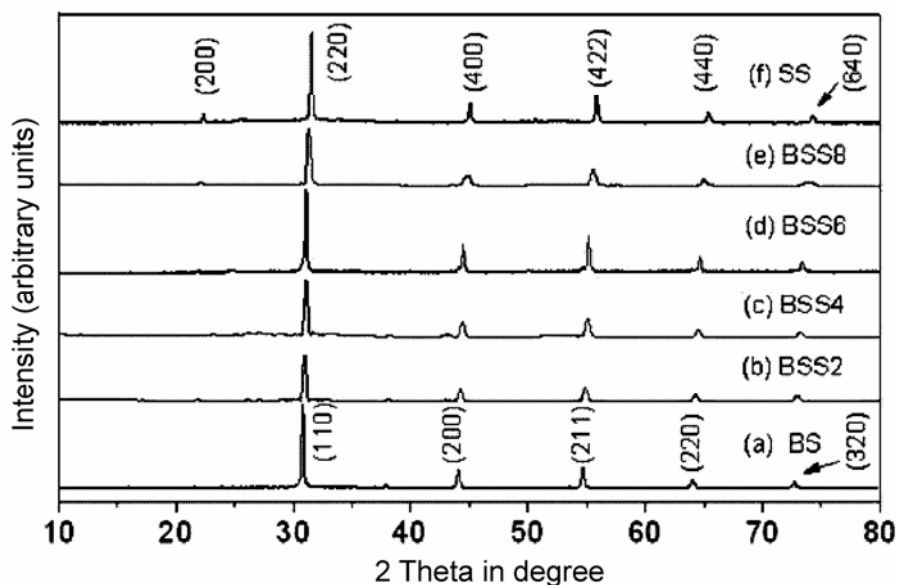
Figure 1. Powder–XRD patterns of $Ba_{1-x}Sr_xSnO_3$ ($x = 0\cdot0$, $0\cdot2$, $0\cdot4$, $0\cdot6$, $0\cdot8$ and $1\cdot0$) synthesized using KOH flux at 400°C for 6 h.

2. Experimental

$Ba_{1-x}Sr_xSnO_3$ ($x = 0–1$) phases were synthesized by MSS using KOH alkali flux as follows. All the chemical reagents used were of analytical grade. $Ba(OH)_2\cdot8H_2O$ (99% powder, Thomas Baker, India), SnO_2 (99·5% powder, Thomas Baker, India), $Sr(NO_3)_2$ (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 CuKα 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 $Ba_{1-x}Sr_xSnO_3$.

Code	Composition	Cubic unit cell parameter (Å)	Volume (Å^3)
BS	$BaSnO_3$	4·110(3)	69·4
BSS2	$Ba_{0\cdot8}Sr_{0\cdot2}SnO_3$	4·101(5)	69·0
BSS4	$Ba_{0\cdot6}Sr_{0\cdot4}SnO_3$	4·085(6)	68·2
BSS6	$Ba_{0\cdot4}Sr_{0\cdot6}SnO_3$	4·078(7)	67·9
BSS8	$Ba_{0\cdot2}Sr_{0\cdot8}SnO_3$	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, $Ba_{1-x}Sr_xSnO_3$ ($x = 0\cdot2$, $0\cdot4$, $0\cdot6$ and $0\cdot8$ 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 pseudo-cubic 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$_2$SnO$_4$

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
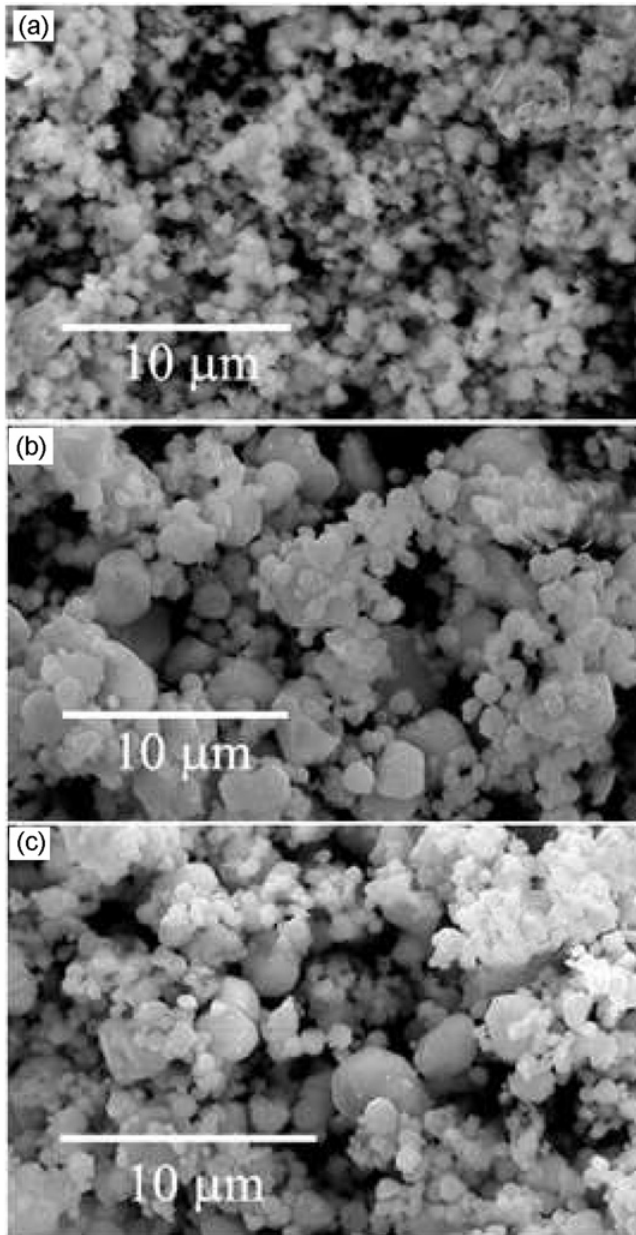
Figure 2. SEM micrographs of BaSnO$_3$ synthesized using KOH flux at 400°C with different soaking durations: (**a**) 6 h, (**b**) 12 h and (**c**) 24 h.
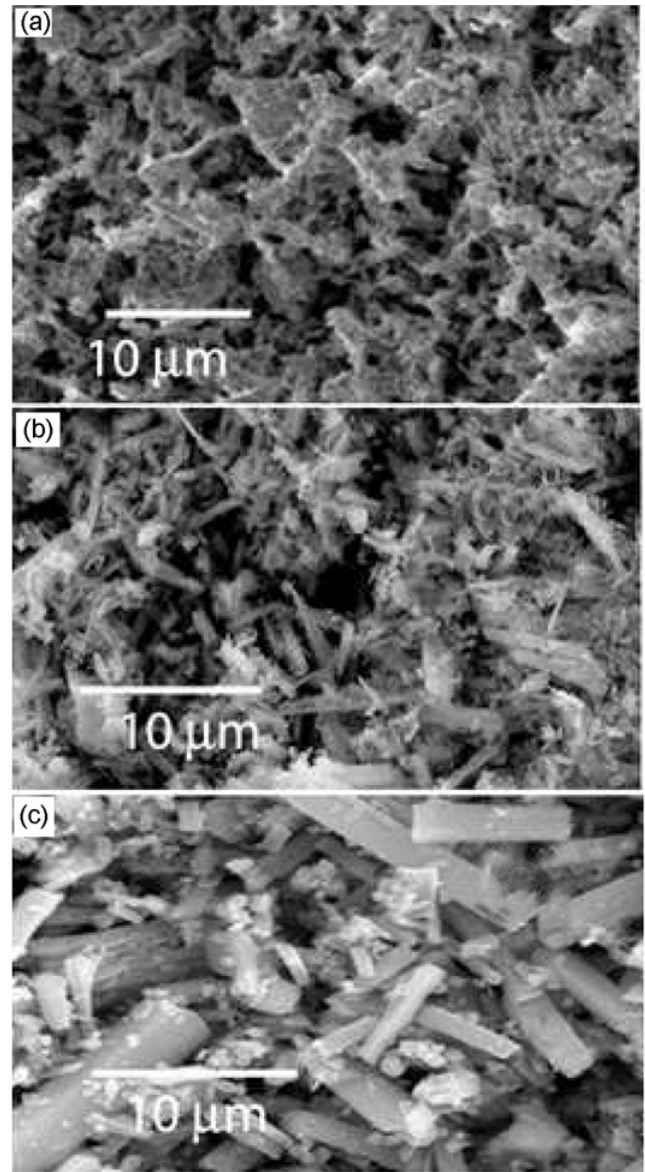
Figure 3. SEM micrographs of SrSnO$_3$ synthesized using KOH flux at 400°C with different soaking durations: (**a**) 6 h, (**b**) 12 h and (**c**) 24 h.
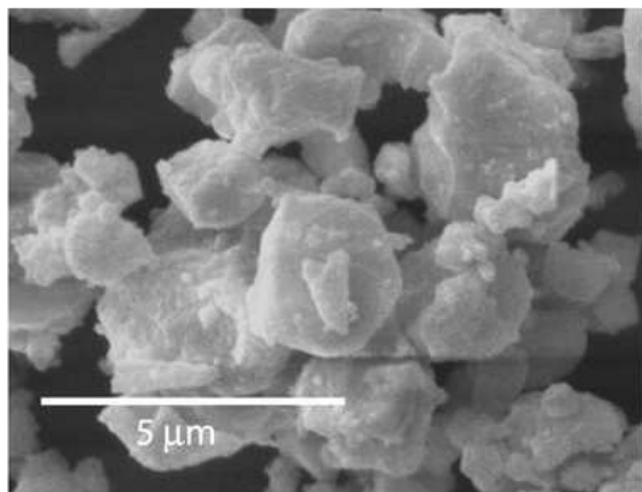
Figure 4. SEM micrograph of BSS5 synthesized using KOH flux at 400°C for 24 h.

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 $Ba_{0.5}Sr_{0.5}SnO_3$ (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 ($Ba_{1-x}Sr_xSnO_3$, $x = 0.0$–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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