

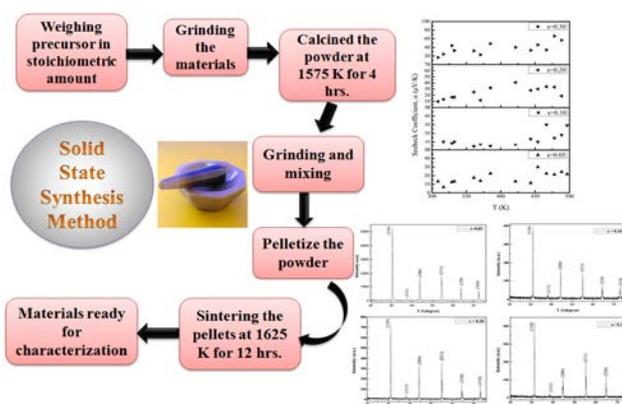
# Investigation on synthesis, structural and electrical properties of Barium Stannate based complex Perovskites $Ba_{1-x}La_xSn_{1-x}Co_xO_3$

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Received on: 5-June-2017, Accepted and Published on: 10-Aug-2017

## ABSTRACT



The effect of La for Ba and Co for Sn substitution on the properties of Barium stannate i.e. solid solution of  $LaCoO_3$  with  $BaSnO_3$  of the type  $Ba_{1-x}La_xSn_{1-x}Co_xO_3$  is investigated for  $x \leq 0.30$ . The powders are prepared using high temperature solid state reaction method for composition  $x \leq 0.30$ . The structural investigations of powders are taken at room temperature by powder X-ray diffractometer. XRD pattern of the samples show the formation of single phase material. Seebeck coefficient is almost constant with temperature and material exhibit p-type conduction. DC conductivity increases with the concentration of  $LaCoO_3$ . Thermally activated small polaron hopping mechanism is the responsible for conduction in these samples.

**Keywords:** Solid state ceramic method, XRD, Seebeck Coefficient, Small polaron hopping mechanism.

## INTRODUCTION

Alkaline-earth Stannates have received considerable attention over past few years because of their potential applications in various fields, such as photo-catalyst, ferromagnet<sup>1</sup>, solid state gas sensors and as anode materials for lithium ion batteries.<sup>2</sup>

Perovskite oxides, with the chemical formula  $ABO_3$ , represent an important, useful, and broad class of materials which includes metals, semiconductors, and insulators displaying a rich variety of

functional properties such as magnetism, piezoelectricity, ferroelectricity, or superconductivity depending on their chemical composition.<sup>3</sup>

$BaSnO_3$  has an ideal cubic perovskite structure belonging to the space group  $Pm3m$  with lattice parameter of 4.12 Å and a wide band gap (3.1 eV) n-type semiconductor. It has excellent thermal stability up to 1000 °C, making it useful as a material for thermally stable capacitors, humidity sensors, gas sensors, and similar high temperature applications.  $BaSnO_3$  is a transparent conducting oxide and the charge carriers in the doped  $BaSnO_3$  have a high mobility.<sup>4,5</sup>

The  $ABO_3$  based perovskite based oxides have good structural flexibility and is able to accommodate a wide range of chemical substitutions making it suitable material for probing correlation between crystal chemistry and physical properties. The major characteristic of perovskites is the possibility for multiple substitutions at the position of the cations within a unit cell the A

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Cite as: *J. Int. Sci. Technol.*, 2017, 5(2), 43-46.

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and B site are crystallo-graphically independent. As a result, there are large groups of compound with different cations at A position ( $A_xA'_{1-x}BO_3$ ); with different cations at B position ( $AB_xB'_{1-x}O_3$ ); and with substitutions at both cationic positions ( $A_xA'_{1-x}B_xB'_{1-x}O_3$ ).<sup>6, 7</sup> Cation substituted at A or B site or both sites simultaneously and its ordering play an important role in mediating structural stability, crystal chemistry and introducing significant modifications in dielectric and ferroelectric properties, magnetic behaviour, electronic and ionic conductivity.

A-site substitution in  $ABO_3$  play a critical role in affecting the properties by lattice distortions associated with size mismatch effect from size difference cation. The substitution at B-site modifies the charge order spin state of ions occupying octahedral site. For perovskite system several researchers have shown that substitutions on both A- and B- sites can produce a large modification in dielectric response and conduction properties.<sup>8-10</sup> For small concentration of substituent, charge compensation occur by electronic compensation i.e. varying valance of ions but for large amount of substituent charge compensate through cation or anion vacancy formation.

Considering the interesting and useful properties of both A- and B-sites substitutions, a similar system with different compositions have been synthesized and studied. The La for Ba and Co for Sn substituted barium Stannate which represents a solid solution between  $BaSnO_3$  and  $LaCoO_3$  of the formula  $Ba_{1-x}La_xSn_{1-x}Co_xO_3$  ( $x \leq 0.30$ ). The perovskite  $LaCoO_3$  is a refractory oxide which exhibits p-type semiconducting and rhombohedral unit cell. It has potential application as catalyst for automotive exhaust gases and a cathode material for high temperature solid state fuel cells. In this system simultaneously substitution of  $La^{3+}$  at  $Ba^{2+}$  site and  $Co^{3+}$  at  $Sn^{4+}$  site is expected to maintain the charge neutrality internally without creation of vacancies at cations or anions sublattice.

## EXPERIMENTAL PROCEDURE

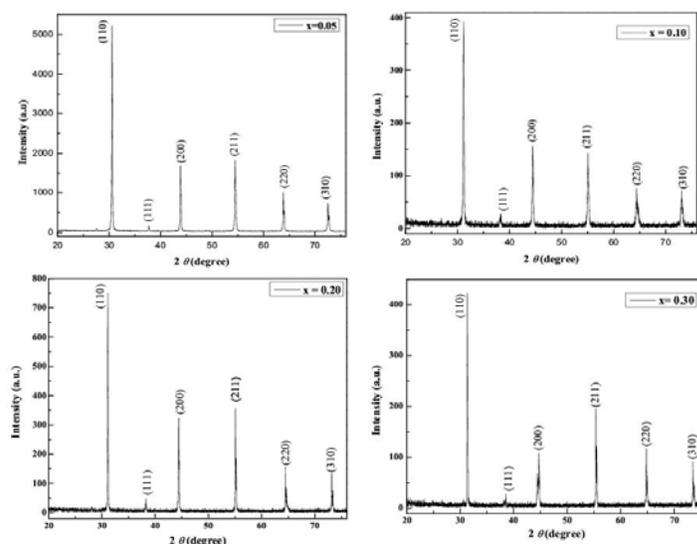
The  $Ba_{1-x}La_xSn_{1-x}Co_xO_3$  ceramic with nominal compositions  $x = 0.05, 0.10, 0.20$  and  $0.30$  were prepared by conventional solid state ceramic method using commercially available analytical grade barium carbonate, lanthanum oxalate, tin di-oxide, and cobalt oxalate, all having purity better than 99.5%, used without further purification. Mixtures of starting materials in appropriate quantity were homogeneously mixed in presence of acetone for 4 hours in mortar pestle. The mixed dry powders were calcined at 1575 K for 4 hours. All these compositions were sintered at 1625 K for 12 hours and then cooled in the furnace slowly. The sintered pellets of all the compositions were powered and powder diffraction patterns were recorded using Rigaku SmartLab (Japan) employing  $Cu-K_\alpha$  radiation. I-V characteristics of the various compositions were studied by applying DC voltage in the range 0-100 V across the samples. Resistivity of the samples was calculated from the slope of I-V plots.

## RESULT AND DISCUSSION

It is found from the X-ray diffraction data that all the compositions in the system show the formation of a single phase

solid solution. The XRD diffraction patterns of all compositions ( $x = 0.05, 0.10, 0.20$  and  $0.30$ ) are give in **Figure-1**. XRD patterns did not contains any line characteristic of the constituents oxides or any other compound (phase) between them. XRD data of all these compositions could be indexed on the basis of simple cubic unit cell similar to  $BaSnO_3$ . It is noted that the lattice parameter 'a' decrease with the value of  $x$ . These decrease if lattice parameter can be understood in terms of the smaller ionic radii of substituent  $La^{3+}$  (1.32 Å) for  $Ba^{2+}$  (1.60 Å) at A-site and  $Co^{3+}$  (0.525 Å or 0.61 Å depending on whether it exists in low spin state  $t_{2g}^6e_g^0$  or high spin state  $t_{2g}^4e_g^2$  respectively) for  $Sn^{4+}$  (0.69 Å) at B-site in  $BaSnO_3$ .<sup>11</sup>

Geometrical density of different compositions calculated from the volume and mass of the sintered pellets are given in **Table-1**. It is noted that the density increase with increase in  $x$ . The decrease of density due to replacement of Sn (atomic weight= 118.69 gm/cm<sup>3</sup>) by Co (atomic weight = 58.93 gm/cm<sup>3</sup>) ions as the atomic weight of Ba (137.34 gm/cm<sup>3</sup>) is very close to that of La (138.91gm/cm<sup>3</sup>) ions. The value of percentage porosity calculated for all samples of the system are given in **Table-1**. Very low value of percentage porosity indicates almost complete sintering of the samples.

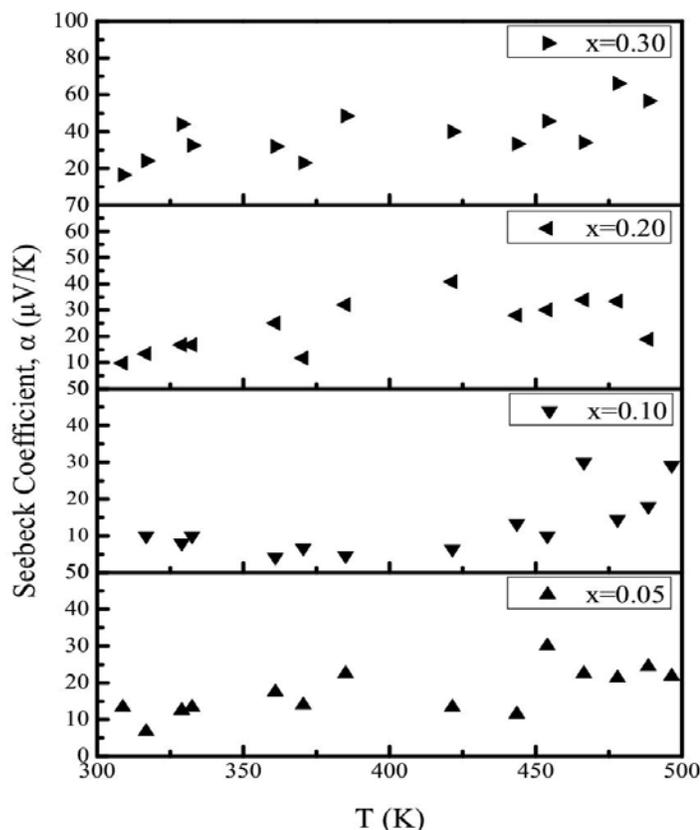


**Figure-1:** XRD of the samples  $Ba_{1-x}La_xSn_{1-x}Co_xO_3$ ;  $x = 0.05, 0.10, 0.20$  and  $0.30$ .

**Table 1:** Variation of different parameters with composition in system,  $Ba_{1-x}La_xSn_{1-x}Co_xO_3$

$x$	Lattice Param eter (Å)	XRD density (gm/cc)	Experi mental density (gm/cc)	Porosit y (%)	Activat ion energy (eV)
0.05	4.12	7.16	7.05	2	0.28
0.10	4.08	7.12	6.93	3	0.28
0.20	4.07	7.07	6.84	3	0.14
0.30	4.05	7.00	6.69	5	0.15

In order to understand the nature of majority charge carriers responsible for conduction in various compositions, Seebeck coefficient ( $\alpha$ ) of all the samples was measured as a function of temperature. Variation of Seebeck coefficient ( $\alpha$ ) with temperature for composition with  $x=0.05, 0.10, 0.20$  and  $0.30$  is shown in Figure-2. Positive values of Seebeck coefficient over the independent of temperature for all compositions. The values of Seebeck coefficient are small and almost equal for all other composition independent of temperature for all compositions.



**Figure 2:** Variation of Seebeck coefficient ( $\alpha$ ) with temperature for composition

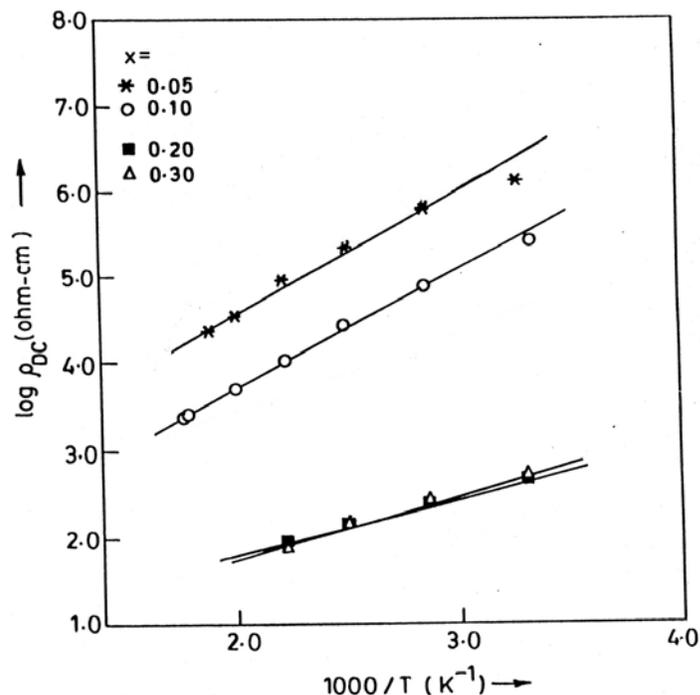
In order to understand the conduction mechanism in this composition, DC resistivity was measured as a function of temperature. A DC voltage was impressed across the sample in the range 0-100 V. Time independent nature of resulting current shows that conduction is predominately electronic in nature in all composition investigated.

Figure-3 is a plot of  $\log \rho_{DC}$  versus inverse of temperature for all compositions. It noted from the plot that the  $\log \rho_{DC}$  is obeying the linear relationship with inverse of temperature given by the equation

$$\rho_{DC} = \rho_0 \exp\left[-\frac{E_a}{kT}\right]$$

Where  $E_a$  is the activation energy for DC conduction,  $k$  is Boltzmann constant and  $T$  is absolute temperature. The activation energies calculated for all compositions using least square fitting of the resistivity data are given in Table-1. It is seen that the value

of activation energy ( $E_a$ ) decrease with increase in  $x$ . For this composition increase in activation energy may be increase due to increase in disorder.



**Figure 3:** Plot of  $\log \rho_{DC}$  versus inverse of temperature for all compositions

In  $\text{LaCoO}_3$  electrical conduction occur via small polaron hopping of charge carriers.<sup>12</sup> In order to confirm that small polaron hopping conduction mechanism is operative in the system  $\text{Ba}_{1-x}\text{La}_x\text{Sn}_{1-x}\text{Co}_x\text{O}_3$ , a number of criteria must be satisfied. A conduction process can be occur by thermally activated hopping of small polaron if the number of charge carriers is constant or varies slowly with temperature but mobility is exponentially depend on temperature.<sup>13</sup> The value of conductivity increases with  $x$  i.e. with the increasing concentration of cobalt ions. This shows that conduction is predominately due to presence of cobalt ions. Increase of cobalt ion; increase the concentration of charge carriers. The activation energy decreases with increases in charge carrier concentration. This behavior is also consistent with small polaron hopping mechanism.<sup>14</sup>

## CONCLUSIONS

- In  $\text{Ba}_{1-x}\text{La}_x\text{Sn}_{1-x}\text{Co}_x\text{O}_3$  system, single solid solution forms over compositions with  $x \leq 0.30$  investigated in the present study.
- XRD patterns shows formation of single phase without presence of any impurity/secondary phases.
- Measurement of Seebeck coefficient shows that these materials exhibit p-type conduction. Seebeck coefficient is almost invariant with temperature.

- DC conductivities increase with increase in concentration of cobalt ions. This shows that cobalt ions play a predominant role in conduction process in these materials.
- Variation of Seebeck coefficient with temperature and composition and variation of DC conductivity with temperature shows that conduction in these samples occurs by thermally activated small polaron hopping mechanism.

## ACKNOWLEDGMENTS

Authors are thankful to Department of Pure and Applied Physics, Guru Ghasidas Vishwavidyalaya and IIT-BHU, Varanasi, India for facilities. One of us (HST) is thankful to UGC, New Delhi for financial assistance through MRP (F. No. 41–954/2012(SR)). MD is thankful to UGC for providing his fellowship.

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