Electrical behaviour of lanthanum- and cobalt-doped strontium stannate

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Abstract. Electrical properties of lanthanum- and cobalt-doped strontium stannate, $SrSnO_3$, have been studied as a function of temperature. All the compositions investigated have cubic structure. Measurement of Seebeck coefficient in one of the cobalt-doped $SrSnO_3$ sample shows that it exhibits p-type conductivity. Results of AC conductivity measurements show that conduction occurs by hopping of charge carriers in lanthanum-doped samples and for $x = 0.01$ in cobalt-doped sample. In $x = 0.05$ sample in cobalt-doped system, conduction seems to occur in extended states.

Keywords. Strontium stannate; electrical properties.

1. Introduction

Titanates, stannates, zirconates, etc. with the general formula ABO_3 ($A = Ca$, Sr, Ba, Pb; $B = Ti$, Sn, Zr) having perovskite structure are useful materials as they find applications in a wide variety of electronic devices (Jaffe *et al* 1971; Lines and Glass 1977; Goodman 1986). Undoped and lanthanum-doped $SrSnO_3$ is used as humidity sensor (Shimizu *et al* 1989). It has been reported that substitution of La^{3+} in Ba^{2+} site in $BaTiO_3$ or Sr^{2+} site in $SrTiO_3$ is compensated by vacancies in Ba^{2+} or Sr^{2+} sublattice respectively for substitutions of more than 1% (Newnham 1983). This is represented by the formula $M_{1-3x/2}La_x(V''_M)_{x/2}TiO_3$ ($M = Ba^{2+}$ or Sr^{2+}). Similarly substitution of Co^{3+} in Ti^{4+} site is compensated by creation of vacancies in oxygen sublattice as represented by the formula $MTi_{1-x}Co_xO_{3-x/2}$ ($M = Ba^{2+}$ or Sr^{2+}). In this paper we report the electrical behaviour of a few compositions of lanthanum- and cobalt-doped strontium stannate prepared by ceramic method.

2. Experimental

Lanthanum- and cobalt-doped strontium stannate samples were prepared by ceramic method using strontium carbonate, lanthanum oxalate, tin(IV) oxide and cobalt oxalate, all having purity better than 99·5%. Lanthanum oxalate was estimated as lanthanum oxide. Appropriate quantities of these materials were accurately weighed, mixed and ground under acetone in an agate mortar for 6 h. The dried powders were transferred to platinum crucibles and calcined at 1473 K for 6 h in air and then cooled to room temperature. The calcined powders were ground, mixed with a few drops of 1% solution of polyvinyl alcohol (PVA) as binder, and pressed as cylindrical pellets. These pellets were slowly heated to 675 K and kept at this temperature for 1 h for complete removal of the binder. The temperature was then raised to 1623 K and the samples were sintered in air at this temperature for 12 h and then cooled slowly.

X-ray diffraction patterns of the crushed pellets were taken using Cu-K_α radiation

in a Rigaku Rotaflex diffractometer. DC resistance was measured as a function of temperature using a Keithley digital electrometer model 616 by two-probe technique. Four-probe technique was used for composition with $x = 0.05$ in the $SrSn_{1-x}Co_xO_3$ system as it had low resistance. Seebeck coefficient (α) was measured on thick sintered cylindrical pellet relative to platinum. AC conductance (G) and dielectric loss (D) were measured as a function of frequency (f) at 350 K using a Hewlett Packard 4192A LF impedance analyser.

3. Results and discussion

Compositions with $x = 0.01$ and 0.05 in the systems $Sr_{1-3x/2}La_xSnO_3$ and $SrSn_{1-x}Co_xO_3$ were synthesized. Powder X-ray diffraction patterns of the various compositions indicate the formation of single-phase solid solution in each case. X-ray data of all the samples could be indexed on the basis of a cubic unit cell similar to $SrSnO_3$ (Parkash *et al* 1994). The values of lattice parameter a for all the compositions are given in table 1. It is observed that a decreases with increasing x in both the systems. This can be understood in terms of ionic radii of Sr^{2+} (1.44 Å), La^{3+} (1.32 Å), Sn^{4+} (0.69 Å) and Co^{3+} (0.61 Å or 0.525 Å depending on whether it exists in the high-spin state $t_{2g}^4 e_g^2$ or low-spin state $t_{2g}^6 e_g^0$) (Shannon and Prewitt 1969).

Variation of Seebeck coefficient α with temperature K of the sample $x = 0.05$ in the $SrSn_{1-x}Co_xO_3$ system is shown in figure 1. The value of α is found to be positive

Table 1. Lattice parameter (a), activation energy (E_a) for DC conductivity and s values for samples in $SrSn_{1-x}Co_xO_3$ and $Sr_{1-3x/2}La_xSnO_3$ systems.

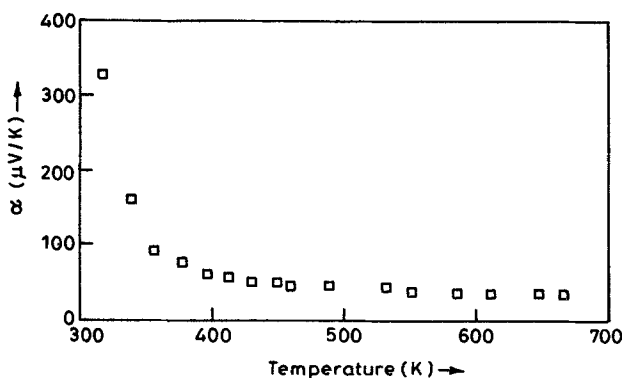| System	x	a(Å)	Activation energy (eV)	s (350 K)
$Sr_{1-3x/2}La_xSnO_3$	0.01	4.026	1.01	0.70
	0.05	4.023	1.07	0.80
$SrSn_{1-x}Co_xO_3$	0.01	4.023	0.54	0.80
	0.05	4.017	0.23	—

Figure 1. Variation of Seebeck coefficient α with temperature in the sample $SrSn_{0.95}Co_{0.05}O_3$.

over the entire temperature range of measurement. This shows that holes are the majority charge carriers. It is observed from figure 1 that α decreases sharply in the temperature range 300–400 K. Thereafter, it remains almost independent of temperature up to 700 K. The p-type behaviour of this composition may be due to generation of holes to compensate for the deficiency of one positive charge in Co^{3+} compared to Sn^{4+}. Measurement of Seebeck coefficient of other samples was not possible due to their high resistance.

Plots of logarithm of DC resistivity (log ρ_{dc}) vs $1000/T$ are shown in figures 2 and 3. The data in figures 2 and 3 were fitted by least-squares method to a straight line and the values of activation energy E_a calculated from the slopes of these lines
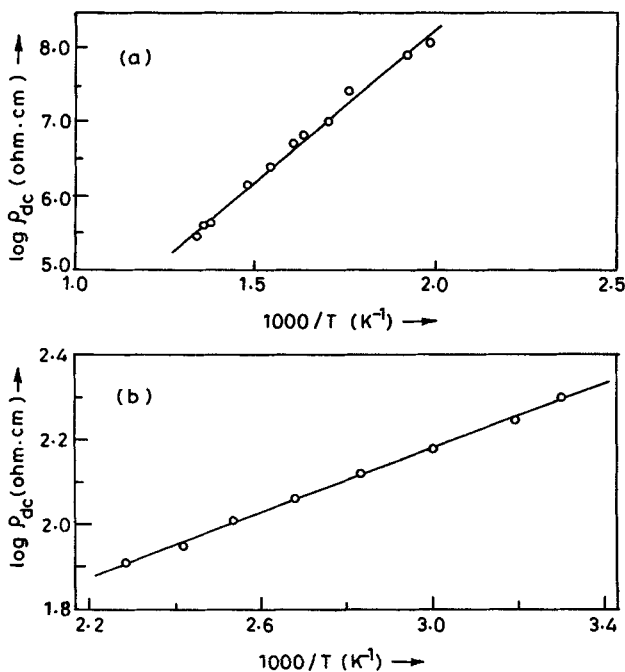

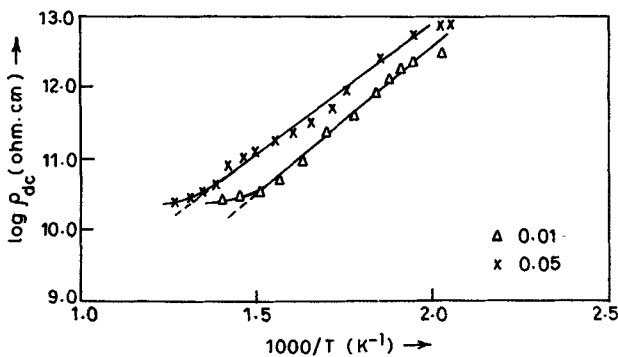**Figure 2.** Plots of $\log \rho_{dc}$ vs $1000/T$ (K^{-1}) for (a) $SrSn_{0.99}Co_{0.01}O_3$ and (b) $SrSn_{0.95}Co_{0.05}O_3$.

Figure 3. Plot of $\log \rho_{dc}$ vs $1000/T$ (K^{-1}) for $Sr_{1-3x/2}La_xSnO_3$.

are given in table 1. The values of activation energy for conduction for the compositions with $x = 0.01$ and 0.05 in the $Sr_{1-3x/2}La_xSnO_3$ system are almost equal (~ 1.00 eV). This shows that the conduction mechanism is the same in both samples. The samples of $SrSn_{1-x}Co_xO_3$ system have different E_a values, much less than those of the lanthanum-doped samples.

The much lower resistivity in the cobalt-doped samples compared to lanthanum-doped samples is due to the difference in the mechanism of compensation in the two cases. In the case of lanthanum-doped strontium stannate, charge compensation occurs due to creation of vacancies in Sr^{2+} sublattice:

$$La_2O_3 \xrightarrow{3SrO} 2La_{Sr}^{\cdot} + V_{Sr}'' + 3O_O.$$ (1)

These strontium ion vacancies do not contribute significantly to the conductivity of these materials because movement of large Sr^{2+} or La^{3+} ions in close-packed oxygen ions is very difficult. On the other hand La^{3+} ions act as impurity scattering centres. This explains the higher resistivity of the samples with $x = 0.05$ compared to $x = 0.01$ in the lanthanum-doped system. On substituting trivalent cobalt in tetravalent tin sites, charge compensation occurs through generation of holes:

$$2Co^{3+} \xrightarrow{2Sn^{4+}} 2Co_{Sn}' + 2h.$$ (2)

The charge compensation is therefore electronic in nature. This accounts for the drastic decrease in resistivity with cobalt substitution. This is in contrast to the ionic compensation which occurs in lanthanum-doped samples.

In order to understand the mechanism of conduction, AC conductivity was measured as a function of frequency in the range $1\,kHz$–$1\,MHz$ at $350\,K$ in the cobalt- ($x = 0.05$) and lanthanum-doped samples. Plots of $\log\sigma_{ac}$ vs $\log f$ are shown in figure 4. It is noted that AC conductivity obeys the relation

$$\sigma_{ac} = Aw^s,$$ (3)

for both the lanthanum-doped samples. Values of s found by least-squares fitting of data are given in table 1. Frequency dependence of AC conductivity in these samples
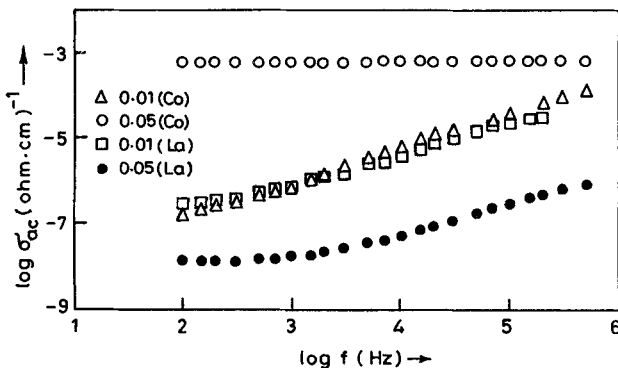

Figure 4. Variation in $\log\sigma_{ac}$ as a function of frequency at $350\,K$ for $SrSn_{1-x}Co_xO_3$ and $Sr_{1-3x/2}La_xSnO_3$ systems.

shows that conduction occurs by hopping of charge carriers among localized sites (Mott and Davis 1979). In lanthanum-doped system these localized sites are associated with Sn^{2+} and Sn^{4+} ions. Traces of divalent Sn^{2+} ions may be present because of loss of oxygen occurring during sintering of these materials at high temperatures in accordance with the reaction (Burn and Neirman 1982)

$$O_O \rightarrow 1/2 O_2 + V_O^{..} + 2e', \tag{4}$$

where all the species are written in accordance with Kröger–Vink notation of defects. The electrons released in the above reaction may be captured by Sn^{4+} to generate Sn^{2+}. Conduction therefore seems to occur by hopping of charge carriers among Sn^{4+} and Sn^{2+} sites in lanthanum-doped samples. In cobalt-doped samples Co^{3+} ions seems to give rise to localized states between the valence band and conduction band. A slight amount of Co^{2+} may be generated due to capture of electrons released in reaction (4). Conduction then seems to occur by excitation of charge carriers at valence band edge and hopping at energies close to it. This mechanism is similar to that found in valence-compensated systems $Ba_{1-x}La_xTi_{1-x}Co_xO_3$, $Ca_{1-x}La_xTi_{1-x}Co_xO_3$ and $Ca_{1-x}Y_xTi_{1-x}Co_xO_3$ (Kumar *et al* 1990; Parkash *et al* 1990; Parkash *et al* 1993). With increasing concentration of cobalt ions in the $SrSn_{1-x}Co_xO_3$ system, the acceptor levels associated with Co^{3+} seem to move closer to the valence band. In the sample with $x = 0.05$, conduction seems to occur by excitation of holes in the valence band. This is confirmed by frequency-independent behaviour of AC conductivity. If conduction occurs in extended states, then the AC conductivity should remain independent of frequency up to 10^7 Hz (Mott and Davis 1979). This is found to be so in the samples with $x = 0.05$ in cobalt-doped samples. Further, the very low value of activation energy E_a in this sample is in conformity with this mechanism.

Acknowledgements

References

Burn I and Neirman S 1982 *J. Mater. Sci.* **17** 3510
Devendra Kumar, Prasad Ch. D and Parkash O 1990 *J. Phys. Chem. Solids* **51** 73
Goodman G 1986 in *Ceramic materials for electronic applications* (ed.) R C Buchanan (New York: Marcel Dekker) p. 79
Jaffe B, Cook Jr W K and Jaffe H 1971 *Piezoelectric ceramics* (London/New York: Academic Press) Ch. 5 and 12
Lines M E and Glass A M 1977 *Principle and applications of ferroelectric and related materials* (Oxford: Clarendon Press) Ch 12
Mott N F and Davis E A 1979 *Electronic processes in non crystalline solids* (Oxford: Clarendon Press) II Ed
Newnham R E 1983 *J. Mater. Educ.* **5** 941
Parkash O, Devendra Kumar, Prasad Ch. D and Tewari H S 1990 *J. Phys. D. Appl. Phys.* **23** 342
Parkash O, Tewari H S, Tare V B and Devendra Kumar 1993 *J. Phys. D. Appl. Phys.* **26** 676
Parkash O, Mandal K D, Christopher C C, Mandalika S Sastry and Devendra Kumar 1994 *J. Mater. Sci. Lett.* (Communicated)
Shimizu Y, Shimalukuro M, Arai H and Seiyama T 1989 *J. Electrochem. Soc.* **136** 1206
Shannon R D and Prewitt C T 1969 *Acta Crystallogr.* **B25** 925