

# Dielectric properties of the $\text{Sr}_{1-x}\text{La}_x\text{Sn}_{1-x}\text{Co}_x\text{O}_3$ system

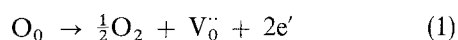
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The possibility of the formation of a solid solution in the  $\text{Sr}_{1-x}\text{La}_x\text{Sn}_{1-x}\text{Co}_x\text{O}_3$  system has been explored. Single-phase solid solution forms in the compositions for  $x \leq 0.10$ . All single-phase solid solution compositions have a cubic structure similar to  $\text{SrSnO}_3$ . The dielectric behaviour of these solid solution compositions has been studied as a function of temperature and frequency. The frequency dependence of dielectric constant and dielectric loss in these materials indicates that space charge polarization contributes significantly to their observed dielectric parameters. Microstructural studies show the presence of well-faceted grains. The average grain size in these samples is small.

## 1. Introduction

Strontium titanate doped with donor ions such as rare-earth or bismuth on the strontium site exhibits relaxor behaviour [1–4]. It becomes semiconducting when sintered in an atmosphere of low oxygen partial pressure. This is due to loss of oxygen from the ceramic at the firing temperature [5, 6] according to the reaction



where all the species are written in accordance with Kröger Vink notation of defects. The presence of donor ions retards the reoxidation of the ceramic grains during cooling from the firing temperature to room temperature [5]. Moreover, insufficient time available during cooling and the decreasing temperature, restrict the reoxidation to the grain boundaries only, making them relatively insulating. However, the grains still remain semiconducting. This gives rise to barrier layers at grain–grain boundary interfaces, imparting very high permittivity to the resulting products. The resistance of the grain boundaries can be increased further by impregnating them with insulating oxides. This is used as a basis for the manufacture of boundary layer capacitors [7].

It has been reported in the recent years that the valence-compensated system  $\text{Sr}_{1-x}\text{La}_x\text{Ti}_{1-x}\text{Co}_x\text{O}_3$  ( $x \leq 0.40$ ) prepared by sintering in air, exhibits the relaxor behaviour characteristic of barrier layers [8]. Some of the compositions have very high values of apparent dielectric constant. This represents a solid solution between  $\text{SrTiO}_3$  and  $\text{LaCoO}_3$ . Simultaneous substitution of  $\text{La}^{3+}$  on  $\text{Sr}^{2+}$  sites and  $\text{Co}^{3+}$  on  $\text{Ti}^{4+}$  sites leads to internal charge compensation in this system. In view of the interesting and useful properties exhibited by this system, attempts have been made to synthesize analogous valence-compensated solid solu-

tion  $\text{Sr}_{1-x}\text{La}_x\text{Sn}_{1-x}\text{Co}_x\text{O}_3$ . In this paper we report the preparation and characterization of the dielectric behaviour of this system prepared by the solid state ceramic method.

## 2. Experimental procedure

Attempts were made to prepare compositions with  $x = 0.00, 0.01, 0.05, 0.10, 0.20, 0.30$  and  $0.50$  in the  $\text{Sr}_{1-x}\text{La}_x\text{Sn}_{1-x}\text{Co}_x\text{O}_3$  system by the conventional ceramic method. The starting materials were strontium carbonate, lanthanum oxalate, tin (IV) oxide and cobalt oxalate, all having a purity better than 99.5%. Lanthanum oxalate was estimated as lanthanum oxide by heating at 1275 K for 4 h. Appropriate quantities of these materials were weighed and mixed using acetone for 6 h in an agate mortar. The dried powders were transferred to platinum crucibles and calcined at 1475 K for 6 h. The calcined powders were ground, mixed with 1% solution of poly vinyl alcohol as binder and pressed into cylindrical pellets. These pellets were heated slowly to 775 K and kept at this temperature for about  $\frac{1}{2}$  h to burn off the binder. The temperature was then raised to 1625 K and the samples were fired at this temperature for 12 h and then cooled slowly. The process of grinding and firing was repeated to improve the chemical homogeneity of the resulting product.

X-ray diffraction patterns of the resulting samples were recorded using  $\text{CuK}_\alpha$  radiation. Microstructures of the freshly fractured surfaces of sintered pellets coated with Au–Pd alloy were observed using a Philips 500 PSEM scanning electron microscope. Capacitance,  $C$ , and dielectric loss,  $D$ , were measured as a function of frequency (0.10 kHz–1 MHz) and temperature (300–500 K) using a Hewlett Packard 4192A LF impedance analyser. As these samples have been

found to be moisture sensitive, the entire cell assembly together with the sample, was first heated to 525 K to drive off any adsorbed moisture. Observations were taken during cooling of the samples at steady temperatures. The observations were then repeated during the heating cycle.

### 3. Results and discussion

From the powder X-ray diffraction (XRD) patterns of the samples, it has been found that solid solution forms only in the compositions with  $x < 0.10$ . Diffraction patterns of the compositions with  $x > 0.10$  were found to contain lines characteristic of constituent oxides. XRD data of the compositions with  $x \leq 0.10$  could be indexed on the basis of a cubic unit cell similar to  $\text{SrSnO}_3$ . The lattice parameter,  $a$ , of these compositions is given in Table I.

Bulk density was calculated from the mass and geometrical dimensions of the pellets. The percentage porosity of the resulting samples calculated from the bulk density and true density is given in Table I. The increase in density with increasing  $x$  is due to increased densification with increasing  $x$ . Scanning electron micrographs of the fractured surfaces of sintered pellets are shown in Fig. 1. The average grain size for various samples calculated from these micrographs by the linear intercept method is also given in Table I. Well-faceted grains are seen in the micrographs of the compositions with  $x = 0.01$  and  $0.05$ . The grain size is small in these materials. Both the acceptor and donor substituents have been reported to segregate to the grain boundaries in oxide perovskites [9]. In our samples,  $\text{La}^{3+}$  and  $\text{Co}^{3+}$  may segregate to the grain boundaries and inhibit grain growth.

Variation of dielectric constant,  $\epsilon_r$ , and dielectric loss,  $D$  as a function of temperature at 1, 10 and 100 kHz for undoped strontium stannate, reported recently, is given in Fig. 2 [10]. Figs 3 and 4 show the variation of  $\epsilon_r$  and  $D$  with temperature for the samples with  $x = 0.01$  and  $0.05$ . Measurement of dielectric properties was not possible in the sample with  $x = 0.10$  owing to its high electrical conductivity. It is observed from Fig. 2a that both dielectric constant and dielectric loss of undoped  $\text{SrSnO}_3$  first decrease sharply up to  $\sim 350$  K. Thereafter, dielectric constant increases slightly with increasing temperature while dielectric loss remains almost constant with temperature. This initial sharp decrease in both these dielectric parameters has been ascribed to loss of adsorbed

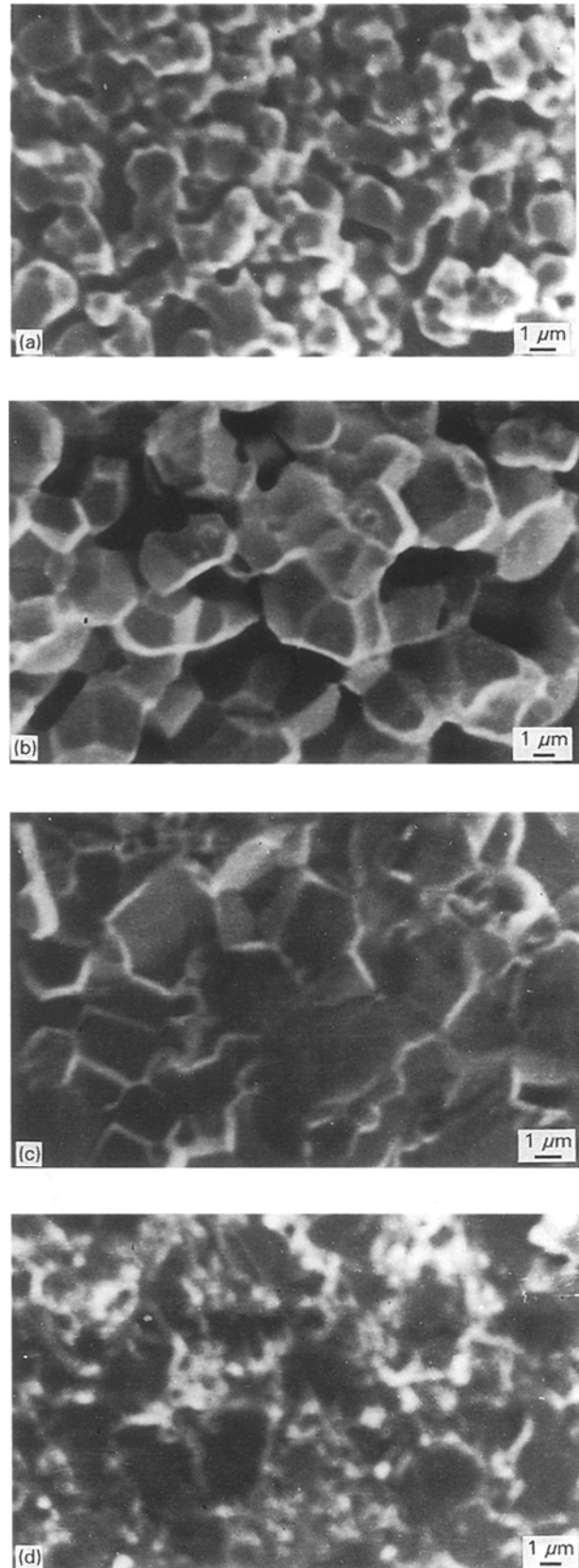


Figure 1 Scanning electron micrographs of the fractured surfaces of various samples in the  $\text{Sr}_{1-x}\text{La}_x\text{Sn}_{1-x}\text{Co}_x\text{O}_3$  system: (a)  $x = 0.00$ , (b)  $x = 0.01$ , (c)  $x = 0.05$ , (d)  $x = 0.10$ .

TABLE I Lattice parameter,  $a$ , grain size, experimental density and percent porosity of various compositions in the system  $\text{Sr}_{1-x}\text{La}_x\text{Sn}_{1-x}\text{Co}_x\text{O}_3$ .

Composition, $x$	Lattice parameter (nm)	Grain size ( $\mu\text{m}$ )	Exp. density ( $\text{g cm}^{-3}$ )	Porosity (%)
0.00	0.4002	2.0	5.21	21.0
0.01	0.4026	2.0	5.45	16.0
0.05	0.4016	3.0	5.99	7.0
0.10	0.4040	3.0	6.02	6.0

moisture on the samples [10]. This is in conformity with the report on the use of strontium stannate as a humidity sensor [11]. These results were reproducible during heating and cooling of the samples.

Dielectric behaviour of the composition with  $x = 0.01$  is essentially similar to that of undoped

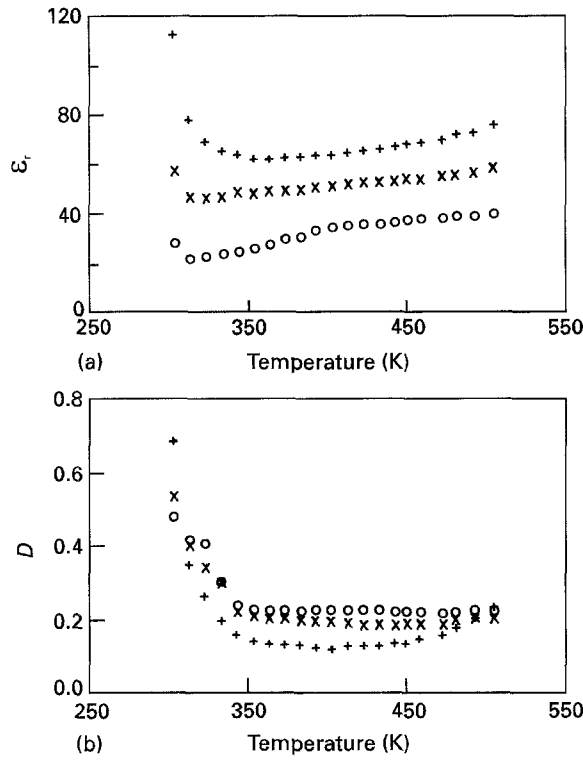


Figure 2 Variation of (a) dielectric constant,  $\epsilon_r$ , and (b) dielectric loss,  $D$ , with temperature of  $\text{SrSnO}_3$ . (+) 1 kHz, (x) 10 kHz, (o) 100 kHz.

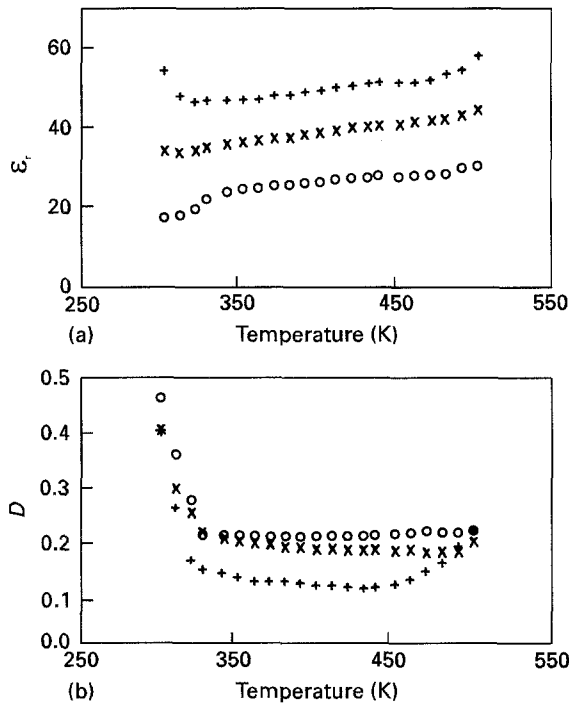


Figure 3 Variation of (a) dielectric constant,  $\epsilon_r$ , and (b) dielectric loss,  $D$ , with temperature for  $\text{Sr}_{0.99}\text{La}_{0.01}\text{Sn}_{0.99}\text{Co}_{0.01}\text{O}_3$ . (+) 1 kHz, (x) 10 kHz, (o) 100 kHz.

sample, i.e.  $\epsilon_r$  and  $D$  remain almost constant with temperature after an initial sharp decrease (Fig. 3a and b). The value of  $\epsilon_r$  in this composition, however, is less than that of  $\text{SrSnO}_3$ .  $\epsilon_r$  versus  $T$  and  $D$  versus  $T$  plots for  $x = 0.05$  are shown in Fig. 4. It is noted that  $\epsilon_r$  increases with temperature and decreases with increasing frequency. The temperature dependence of

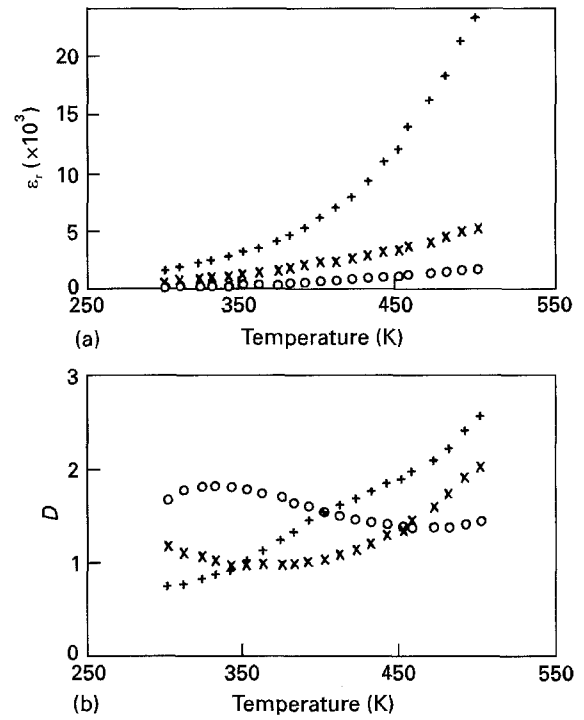


Figure 4 Variation of (a) dielectric constant,  $\epsilon_r$ , and (b) dielectric loss,  $D$  with temperature for  $\text{Sr}_{0.95}\text{La}_{0.05}\text{Sn}_{0.95}\text{Co}_{0.05}\text{O}_3$ . (+) 1 kHz, (x) 10 kHz, (o) 100 kHz.

$\epsilon_r$  becomes stronger at higher temperature and decreasing frequency. The dielectric constant for this composition is much higher than that of  $x = 0.00$  and  $0.01$  samples.

A very broad peak is observed in the  $D$  versus  $T$  plot at 100 kHz around 350 K for this composition. This indicates the presence of a relaxation process. This is clearly illustrated in Fig. 5a and b where  $D$  versus  $\log f$  has been plotted for  $x = 0.01$  and  $0.05$ . A peak is observed in these plots which is much more pronounced in  $x = 0.05$  than  $x = 0.01$ . This peak shifts to higher frequency with increasing temperature. This is because a peak is observed when  $\omega\tau = 1$  where  $\omega$  the angular frequency is equal to  $2\pi f$ ,  $f$  being the frequency ( $\text{cycles}^{-1}$ ) and  $\tau$  is the relaxation time. With increase in temperature,  $\tau$  decreases and therefore the relation  $\omega\tau = 1$  will be satisfied at higher frequency. Relaxation time,  $\tau$ , was determined from the peak position at different temperatures. Log  $\tau$  has been plotted as a function of inverse of temperature in Fig. 6. It is noted that this plot is linear. This shows that  $\tau$  follows the Arrhenius relationship

$$\tau = \tau_0 \exp E_a/kT \quad (2)$$

where  $E_a$  is the activation energy for the relaxation process. Value of  $E_a$  determined from the slope of the line in Fig. 6 is 0.14 eV. This relaxation process may be associated with reorientation of dipoles as explained below.

These materials are expected to lose traces of oxygen in accordance with reaction 1. The electrons released may be captured by  $\text{Sn}^{4+}$  ions to generate  $\text{Sn}^{2+}$  ions.  $\text{Sn}^{2+}$  ions on  $\text{Sn}^{4+}$  sites will form dipoles with vacant oxygen sites, namely  $[\text{Sn}_{\text{Sn}^{4+}}^{2+}]^{\prime}\text{V}_\text{O}$ . These dipoles can change their orientation owing to jumping of oxygen ions into vacant oxygen sites.

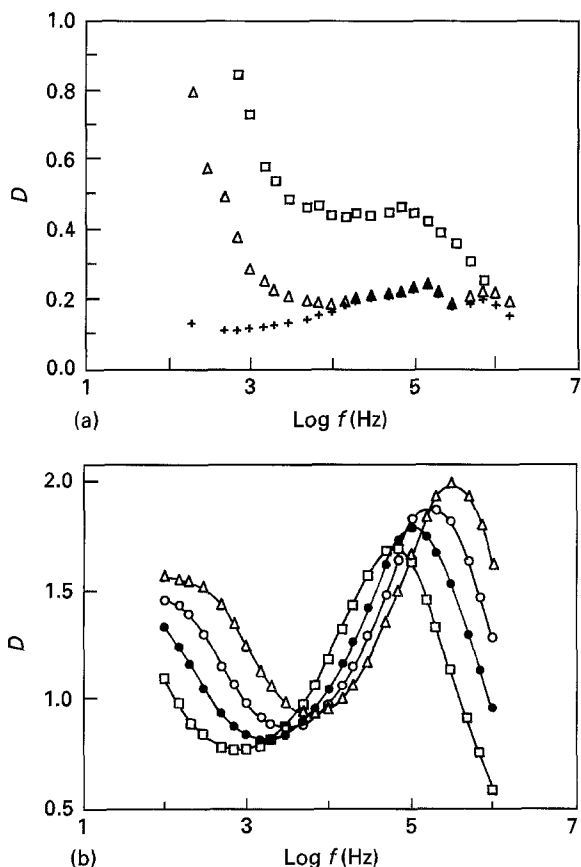


Figure 5 Plots of dielectric loss,  $D$  versus  $\log f$  for the compositions with (a)  $x = 0.01$  and (b)  $x = 0.05$  in the system  $\text{Sr}_{1-x}\text{La}_x\text{Sn}_{1-x}\text{Co}_x\text{O}_3$ . (a) ( $\square$ ) 300 K, (+) 400 K, ( $\Delta$ ) 500 K. (b) ( $\square$ ) 300 K, ( $\bullet$ ) 325 K, ( $\circ$ ) 350 K, ( $\Delta$ ) 375 K.

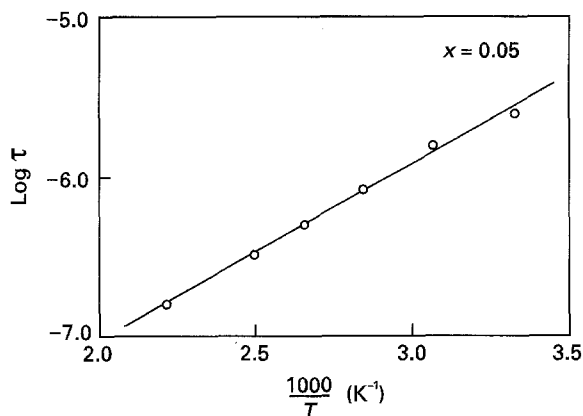


Figure 6 Plot of relaxation time,  $\tau$ , versus  $1000/T$  for the sample  $\text{Sr}_{0.95}\text{La}_{0.05}\text{Sn}_{0.95}\text{Co}_{0.05}\text{O}_3$ .

Strong frequency dependence of the dielectric constant in this composition shows that interfacial polarization contributes significantly to the polarization in this sample. Interfacial polarization arises whenever phases with different conductivities are present. In these materials, prepared by a slow diffusion controlled thermochemical process, there are always microheterogeneities present due to random occupation of equivalent sites by different ions. In the present case, octahedral sites are occupied randomly by  $\text{Sn}^{4+}$  and  $\text{Co}^{3+}$  ions. Similarly dodecahedral sites are occupied by  $\text{La}^{3+}$  and  $\text{Sr}^{2+}$  ions. Because of these chemical microheterogeneities, samples have different microregions with varying conductivity. These microregions give rise to interfacial polarization.

### Acknowledgements

Financial support from the Department of Science and Technology, Government of India, New Delhi is gratefully acknowledged. One of the authors (K.D.M.) thanks CSIR, New Delhi, for awarding a Research Associateship.

### References

1. D. W. JOHNSON, L. E. CROSS and F. A. HUMMEL, *J. Appl. Phys.* **41** (1970) 2828.
2. J. BOUWMA, K. J. DeVRIES and A. J. BURGRAAF, *Phys. Status Solidi (a)* **35** (1976) 281.
3. G. I. SKANVI and E. N. MATVEENA, *Sov. Phys.* **3** (1957) 905.
4. L. E. CROSS, *Proc. Inst. Elect. Eng.* **109** (1962) 407.
5. I. BURN and S. NEIRMAN, *J. Mater. Sci.* **17** (1982) 3510.
6. S. NEIRMAN and I. BURN, *ibid.* **19** (1984) 737.
7. N. YAMAOKA, *Bull. Am. Ceram. Soc.* **65** (1986) 1149.
8. OM PARKASH, CH. DURGA PRASAD and DEVENDRA KUMAR, *J. Mater. Sci.* **25** (1990) 487.
9. S. B. DESU and D. A. PAYNE, *J. Am. Ceram. Soc.* **73** (1990) 3407.
10. OM PARKASH, K. D. MANDAL, C. C. CHRISTOPHER, MANDALIKA S. SASTRY and DEVENDRA KUMAR, *J. Mater. Sci. Lett.* **13** (1994) 1616.
11. Y. SHIMIZU, M. SHIMALUKURO, H. ARAI and T. SEIYAMA, *J. Electrochem. Soc.* **136** (1989) 1206.

Received 19 April 1994

and accepted 13 February 1996