

# Preparation, structure and dielectric properties of the system $\text{Sr}_{1-x}\text{La}_x\text{Ti}_{1-x}\text{Ni}_x\text{O}_3$

OM PARKASH, LAKSHMAN PANDEY, MUKHESH KUMAR SHARMA, DEVENDRA KUMAR\*

*School of Materials Science and Technology, and \*Department of Ceramic Engineering, Institute of Technology, Banaras Hindu University, Varanasi 221 005, India*

Attempts have been made to synthesize the solid solution  $\text{Sr}_{1-x}\text{La}_x\text{Ti}_{1-x}\text{Ni}_x\text{O}_3$  for  $x \leq 0.50$  and its electrical behaviour has been studied. It was found that a solid solution forms for compositions up to  $x = 0.10$ . The structure remained cubic. These compositions exhibited dielectric relaxator behaviour. The average grain size in these materials was very small.

## 1. Introduction

Strontium titanate doped with donor ions such as rare earth or bismuth ions on strontium sites exhibits relaxator behaviour [1-4]. It becomes semiconducting when sintered in atmospheres of low oxygen partial pressure, exhibiting barrier layer capacitor behaviour [5]. This is due to loss of oxygen from the ceramic at the firing temperature. Owing to insufficient time available during the cooling, reoxidation of the grain boundaries only takes place making them insulating enveloping semiconducting grains. This leads to the development of barriers at the grain-grain boundaries interface imparting a very high dielectric constant to the resulting materials which increases with increasing grain size.

Attempts have been made over the last few years in our laboratory to synthesize and characterize various valence-compensated solid solutions. The systems  $\text{Pb}_{1-x}\text{La}_x\text{Ti}_{1-x}\text{Co}_x\text{O}_3$ ,  $\text{Na}_{1-x}\text{La}_x\text{Nb}_{1-x}\text{Co}_x\text{O}_3$  have been prepared and their electrical properties studied [6-10]. In these systems, simultaneous substitutions of suitable heterovalent ions at both the sites maintains the electrical charge neutrality. It has been found that the solid solution forms over the entire composition range in the above systems and they exhibit interesting electrical and dielectric properties, e.g. compositions with  $0.10 \leq x \leq 0.50$  exhibit relaxator behaviour in the system  $\text{Pb}_{1-x}\text{La}_x\text{Ti}_{1-x}\text{Co}_x\text{O}_3$  [8]. The above systems are basically solid solutions of  $\text{LaCoO}_3$  with  $\text{PbTiO}_3$  and  $\text{NaNbO}_3$ , respectively. In this paper, we report the dielectric properties of another valence-compensated system,  $\text{Sr}_{1-x}\text{La}_x\text{Ti}_{1-x}\text{Ni}_x\text{O}_3$ , which is a solid solution of  $\text{SrTiO}_3$  with  $\text{LaNiO}_3$ .  $\text{LaNiO}_3$  exhibits metallic conductivity and Pauli-paramagnetism [11]. This is the first report on this system to the best of our knowledge.

## 2. Experimental procedure

All the samples ( $x = 0.01, 0.03, 0.05, 0.10, 0.15, 0.20, 0.30$  and  $0.50$ ) were prepared by the ceramic method using strontium oxalate,  $\text{La}_2(\text{C}_2\text{O}_4)_3 \cdot n\text{H}_2\text{O}$ , basic nickel carbonate and  $\text{TiO}_2$  and having a purity of 99.5%. Lanthanum oxalate and strontium oxalate

were estimated as lanthanum oxide and strontium carbonate, respectively. Appropriate quantities of these materials were weighed and mixed in an agate mortar using acetone. The dried powders were transferred to platinum crucibles and calcined at 1523 K for 12 h and furnace cooled. The calcined powders were ground, mixed with 1% solution of polyvinyl alcohol as binder and pressed into cylindrical pellets. These pellets were heated slowly to 873 K and kept at this temperature for about  $\frac{1}{2}$  h to burn off the binder. The temperature was then raised to 1573 K and the samples were fired at this temperature for 24 h and then cooled in the furnace.

X-ray diffraction (XRD) patterns of the resulting samples were taken using  $\text{CuK}\alpha$  radiation in a Jeol diffractometer. The bulk density of the sintered pellets was determined from the mass and geometrical dimensions. Porosity was calculated from the bulk and true density. Microstructures of freshly fractured surfaces of sintered pellets coated with gold were observed using a Philips 500 PSEM scanning electron microscope. For dielectric measurements, both the surfaces of sintered pellets were polished smooth and coated with air-dried silver paint. Capacitance and dielectric loss were measured as a function of frequency in the range 100 Hz to 1 MHz in the temperature range 300 to 575 K.

## 3. Results and discussion

X-ray diffraction (XRD) patterns of the samples with  $x \leq 0.10$  did not contain lines characteristic of constituent oxides indicating the formation of solid solution in these compositions. Compositions with  $x \leq 0.15$  were found to contain XRD lines characteristic of constituent oxides in their diffraction patterns indicating the presence of unreacted oxides in them. We have characterized only the compositions with  $x \leq 0.10$  which are single-phase materials. X-ray diffraction patterns of all four compositions could be indexed on the basis of a cubic unit cell similar to  $\text{SrTiO}_3$ . The lattice parameter,  $a$ , for these compositions is given in Table I. It is found that the lattice parameter does not change with  $x$ . This is because the

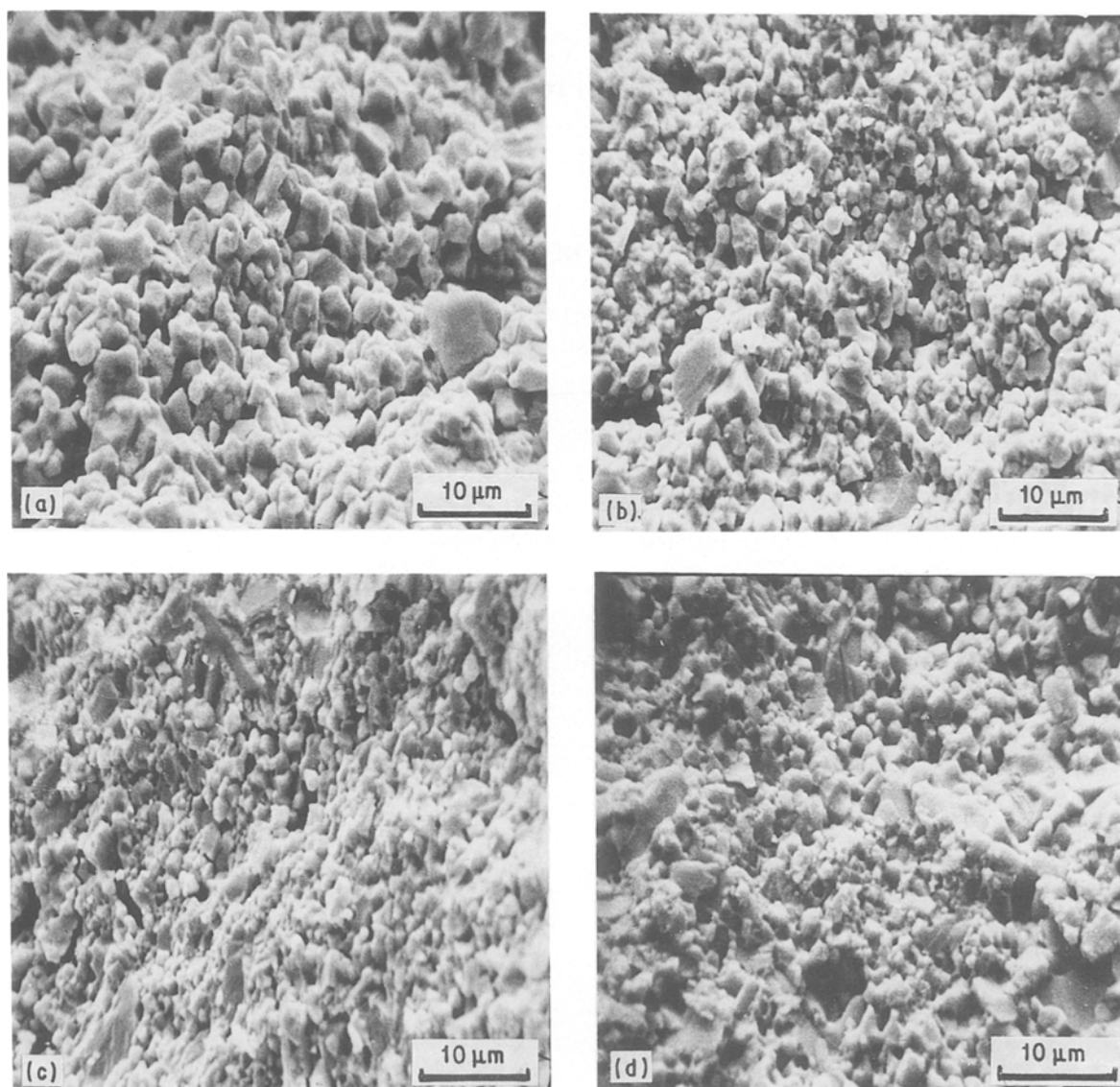


Figure 1 Scanning electron micrographs of the various compositions, (a)  $x = 0.01$ , (b)  $x = 0.03$ . (c)  $x = 0.05$  and (d)  $x = 0.10$ , in the system  $\text{Sr}_{1-x}\text{La}_x\text{Ti}_{1-x}\text{Ni}_x\text{O}_3$ .

ionic radii of  $\text{La}^{3+}$  and  $\text{Ni}^{3+}$  are almost equal to the ionic radii of  $\text{Sr}^{2+}$  and  $\text{Ti}^{4+}$ , respectively.

Bulk density and per cent porosity of all the samples are given in Table I. Increase of bulk density with  $x$  is due to replacement of strontium and titanium by heavier lanthanum ions, and nickel respectively. Sinterability decreases with  $x$ . Scanning electron micrographs of the fractured surfaces of sintered pellets are shown in Fig 1. Average grain size determined from these micrographs is given in the last column of Table I. The grain size is small in these materials. This can be explained as follows.

The presence of  $\text{La}^{3+}$  ions, which act as donors

at  $\text{Sr}^{2+}$  sites, facilitates the loss of oxygen during the sintering [5]. Similarly, the presence of acceptor ions such as nickel at a titanium site also favours the formation of oxygen vacancies to maintain the electrical charge neutrality [12]. Hence simultaneous substitution of  $\text{La}^{3+}$  at  $\text{Sr}^{2+}$  and  $\text{Ni}^{3+}$  at  $\text{Ti}^{4+}$  sites produces oxygen-deficient materials. These oxygen vacancies are charged and segregate at the grain boundaries. The presence of these charged oxygen vacancies at grain boundaries attracts other substituted ions (such as  $\text{Ni}^{3+}$ ) to the grain boundaries which inhibit the grain growth and densification process. The results are similar to

TABLE I Lattice parameter,  $a$ , bulk density, percentage porosity, average grain size and dielectric constant,  $\epsilon$ , at 1 kHz and 300 K using silver and nickel paint of various samples in the system  $\text{Sr}_{1-x}\text{La}_x\text{Ti}_{1-x}\text{Ni}_x\text{O}_3$

$x$	$a$ (nm)	Bulk density ( $\text{g cm}^{-3}$ )	% porosity	Average grain size ( $\mu\text{m}$ )	$\epsilon$	
					Silver paint	Nickel paint
0.01	0.3905	4.36	15	4.2	160	142
0.03	0.3903	4.37	16	3.5	162	134
0.05	0.3900	4.72	10	2.7	176	143
0.10	0.3904	4.76	10	3.1	211	182

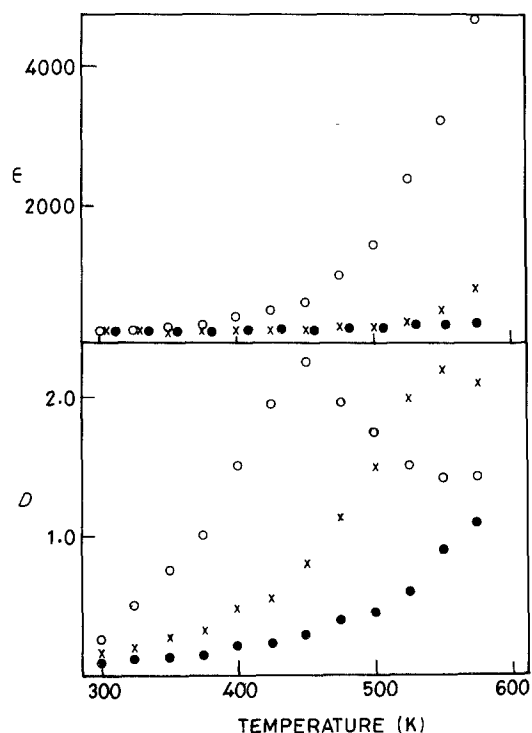


Figure 2 Variation of relative dielectric constant,  $\epsilon$ , and dielectric loss,  $D$ , for the composition with  $x = 0.03$  at various frequencies: (O) 1 kHz, (x) 10 kHz, (●) 100 kHz.

those obtained in the case of cobalt-doped barium titanate [13].

Typical plots of the relative dielectric constant,  $\epsilon$ , and dielectric loss,  $D$ , at a few frequencies as a function of temperature are shown in Figs 2 and 3. The behaviour of the compositions with  $x = 0.01$  and  $0.03$  is essentially similar. Similarly, the behaviour of the composition with  $x = 0.05$  is similar to that of the composition with  $x = 0.10$ . In the sample with  $x = 0.01$  and  $0.03$ ,  $\epsilon$  is temperature and frequency independent up to a particular temperature,  $T_a$ , and thereafter it increases very rapidly. Frequency dependence also becomes very much pronounced above  $T_a$ . The variation of  $D$  with  $T$  is essentially similar to that of  $\epsilon$  with  $T$  for the composition with  $x = 0.01$ .  $D$ - $T$  plots for the sample with  $x = 0.03$  show a peak at a particular temperature which shifts to the higher side with increasing frequency.

$\epsilon$ - $T$  and  $D$ - $T$  plots of the compositions with  $x = 0.05$  and  $0.10$  show rounded peaks which shift to higher temperature with increasing frequencies. Peak temperatures are different for  $\epsilon$ - $T$  and  $D$ - $T$  plots. Further dielectric parameters ( $\epsilon$  and  $D$ ) show frequency dependence which becomes very pronounced near the peak temperatures. These fractures indicate that these materials exhibit relaxator behaviour. Samples with  $x = 0.01$  and  $0.03$  may also exhibit peaks in their  $\epsilon$ - $T$  plots at higher temperatures.

A peak is observed in the  $D$ - $T$  plots when the relation  $\omega\tau = 1$  is satisfied where  $\omega = 2\pi f$ ;  $f$  is the frequency and  $\tau$  is the characteristic relaxation time. As  $T$  increases,  $\tau$  decreases and hence the peak temperature increases with increasing frequency. This is characteristic of Debye relaxation. Fig. 4 shows typical  $\epsilon$ - $\log f$  and  $D$ - $\log f$  plots of the system

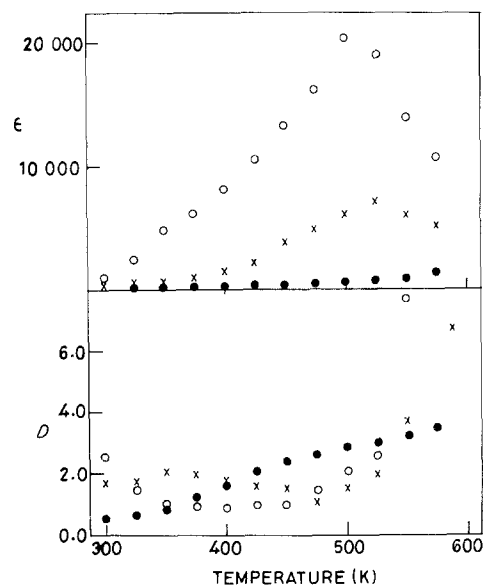


Figure 3 Variation of relative dielectric constant,  $\epsilon$ , and dielectric loss,  $D$ , for the composition with  $x = 0.10$  at various frequencies in the system  $\text{Sr}_{1-x}\text{La}_x\text{Ti}_{1-x}\text{Ni}_x\text{O}_3$ , (O) 1 kHz, (x) 10 kHz, (●) 100 kHz.

$\text{Sr}_{1-x}\text{La}_x\text{Ti}_{1-x}\text{Ni}_x\text{O}_3$ . Shifting of the peak in  $D$ - $\log f$  plots to the higher frequency side with increasing temperature confirms the relaxation polarization in these materials.

It is also seen that the dielectric constant decreases sharply with frequency up to the peak frequency (in the  $D$ - $\log f$  plots) and thereafter remains almost constant with frequency. This shows that space charge polarization contributes significantly to the observed dielectric properties. Space charge polarization arises due to the presence of chemical heterogeneities at the microlevel in these materials. These heterogeneities

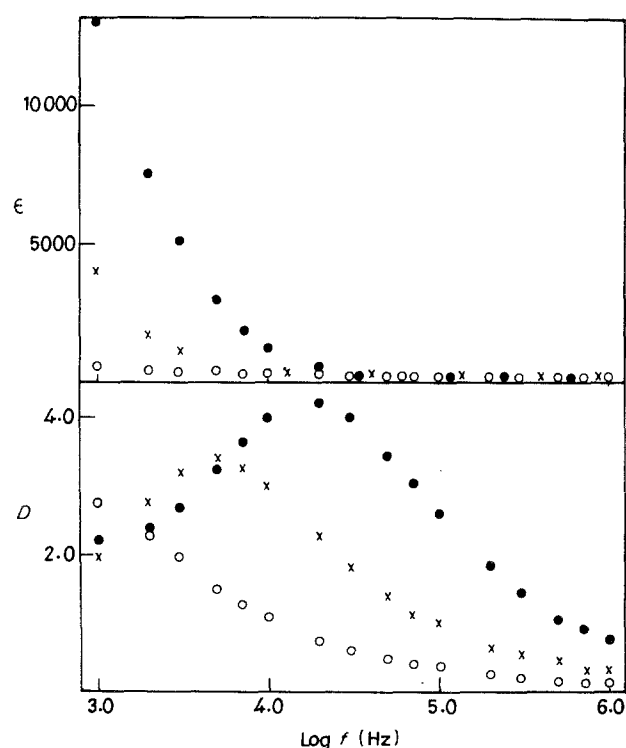


Figure 4 Plots of  $\epsilon$  against  $\log f$  and  $D$  against  $\log f$  for the composition with  $x = 0.05$  in the system  $\text{Sr}_{1-x}\text{La}_x\text{Ti}_{1-x}\text{Ni}_x\text{O}_3$  at various temperatures: (O) 350 K, (x) 450 K, (●) 550 K.

exist due to limitations of slow diffusion-controlled thermochemical ceramic process used for their preparation. The presence of these microheterogeneities gives rise to regions with different conductivity resulting in space charge polarization. Dielectric constant increases with  $x$  which can be understood in terms of the increasing space-charge polarization with increasing  $x$ .  $D$  also increases with  $x$ . This can largely be attributed to the increasing d.c. conductivity with nickel ions concentration (i.e. with  $x$ ). Values of  $\epsilon$  at 1 kHz and 300 K are given in Table I for the various samples.

Dielectric measurements were also made on the same pellets after removing the silver paint by grinding and washing in iso-amyl acetate and then applying air-dried nickel paint, causing minimum change in the dimensions of the pellet. Values of dielectric constant at 1 kHz and 300 K are given in Table I together with the values observed with silver paint. Any dependence of dielectric constant on the dimensions of samples and microstructure have been eliminated by using the same pellet. The data in Table I show that the dielectric constant depends on the electrode material. This is characteristic of the relaxator materials [5]. The value of the dielectric constant observed in these materials is much less than that usually observed in the case of relaxator materials. This is due to their very small grain size. We are synthesizing these materials under different atmospheres in order to study the effect of sintering atmospheres on their properties. The results of these investigations will be reported elsewhere.

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