

## Dielectric and conductivity properties of lanthanum-modified strontium copper niobate

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A number of compounds with perovskite structure exhibit ferroelectricity. Barium titanate, one of the important ferroelectric materials for device applications [1], has a relatively low Curie temperature ( $T_c$ ) of 120 °C. In order to alter the Curie point to higher or lower temperatures, solid solutions are usually formed by judicious selection of suitable substituents either in Ba or in Ti sites. For instance, modest amounts of  $Pb^{2+}$  in  $BaTiO_3$  raise its  $T_c$  whereas  $Sr^{2+}$  for Ba or Zr for Ti lowers the  $T_c$  [2–4]. Investigations on the synthesis of new perovskite-type compounds led to the unravelling of many compositions [5–7], some of which, particularly copper-containing Perovskites [6], were found to exhibit higher Curie temperatures in the range 300–1200 °C. Since the ferroelectric phase transition is connected with the electron–phonon interaction which takes place in the presence of the Jahn–Teller pseudo-effect, this is very pronounced in compounds containing bivalent copper of  $3d^9$  electron configuration. Strontium copper niobate [ $Sr(Cu_{1/3}Nb_{2/3})O_3$  (SCN)] crystallizes in a tetragonal symmetry with lattice parameters  $a = 0.3944$  nm and  $c = 0.4074$  nm, and is also reported to be a ferroelectric material with Curie temperature of 390 °C [6]. No further studies on SCN have appeared in the literature. In this letter we report the synthesis, characterization and the effect of partial substitution of lanthanum on the dielectric and conductivity properties of SCN.

Samples of SCN and lanthanum-incorporated strontium copper niobate (La-SCN) were prepared by the usual ceramic method with  $SrCO_3$ ,  $CuO$ ,  $Nb_2O_5$  and  $La_2O_3$  of AR grade purity as starting materials. Stoichiometric quantities of these materials are taken to yield the compositions  $(Sr_{1-x}La_{2x/3})(Cu_{1/3}Nb_{2/3})O_3$  with  $x = 0.0, 0.075, 0.150, 0.225$  and  $0.300$ . The physical mixtures were dry ground into fine powders and these were further mixed thoroughly in presence of alcohol to improve the homogeneity. The mixtures were calcined twice at 950 °C for 4 h. The calcined samples were pressed into pellets with 5% poly(vinyl acid) as binder using a pressure of 4.5 tonne  $in^{-2}$  (68 MPa). The pelletized samples were sintered at 1200 °C for 6 h. The phase identification was followed by X-ray diffraction (XRD) using  $CuK_\alpha$  radiation. The dielectric

measurements were done at 1 kHz using a capacitance bridge, digital LCR meter (type VLCR6). D.c. resistivity measurements on these samples were performed by the two-probe method with a ECIL electrometer amplifier (type EA815) using a d.c. voltage of 10 V. Silver-coated pellets were used for the above studies.

From the XRD data, SCN and La-SCN samples were found to be monophasic and tetragonal in symmetry in accordance with earlier reports [6, 7]. The lattice parameters for these samples are given in Table I. As can be seen from the XRD data in Table I, substitution of La for Sr seems to promote the tetragonal distortion.

Fig. 1 shows the temperature ( $T$ ) dependence of the dielectric constant ( $\epsilon$ ) of SCN and La-SCN samples. As can be seen, increased substitution of  $Sr^{2+}$  by  $La^{3+}$  resulted in a reduction of the Curie temperature, from 345 to 245 °C, with an increase in peak dielectric constant from 255 to 1439. Furthermore, higher polarization ( $\alpha$ ) of La might be responsible for the enhanced dielectric constant [ $\alpha(Sr^{2+}) = 0.86$  and  $\alpha(La^{3+}) = 1.08$ ]. Similar behaviour was reported for other systems [8] such as  $Ba(Ti_{1-x}Zr_x)O_3$ . Since the maximum value of  $\epsilon$  at the Curie point  $T_c$  in an ideal ferroelectric crystal can be described by the Curie–Weiss law,  $\epsilon = C/(T - T_c)$  for  $T > T_c$ . The Curie constant ( $C$ ) can be obtained from the temperature dependence of  $\epsilon$  at  $T > T_c$ . The estimated Curie constants for these samples are given in Table II, together with the respective Curie temperatures, room-temperature dielectric constant ( $\epsilon_{RT}$ ) and peak dielectric constant ( $\epsilon_{TC}$ ).

Fig. 2 shows the variation of resistivity ( $\rho$ ) with temperature for SCN and La-SCN. These samples show resistivity maxima at temperatures ( $\rho_T$ ) which

TABLE I Lattice parameters of the SCN and La-SCN samples

Sample	$a$ (nm)	$c$ (nm)	$c/a$
$Sr(Cu_{1/3}Nb_{2/3})O_3$	0.392 63	0.411 81	1.046
$(Sr_{0.975}La_{0.05})(Cu_{1/3}Nb_{2/3})O_3$	0.392 85	0.412 28	1.049
$(Sr_{0.850}La_{0.10})(Cu_{1/3}Nb_{2/3})O_3$	0.385 39	0.420 58	1.091
$(Sr_{0.775}La_{0.15})(Cu_{1/3}Nb_{2/3})O_3$	0.386 29	0.423 15	1.095
$(Sr_{0.700}La_{0.20})(Cu_{1/3}Nb_{2/3})O_3$	0.381 06	0.420 25	1.102

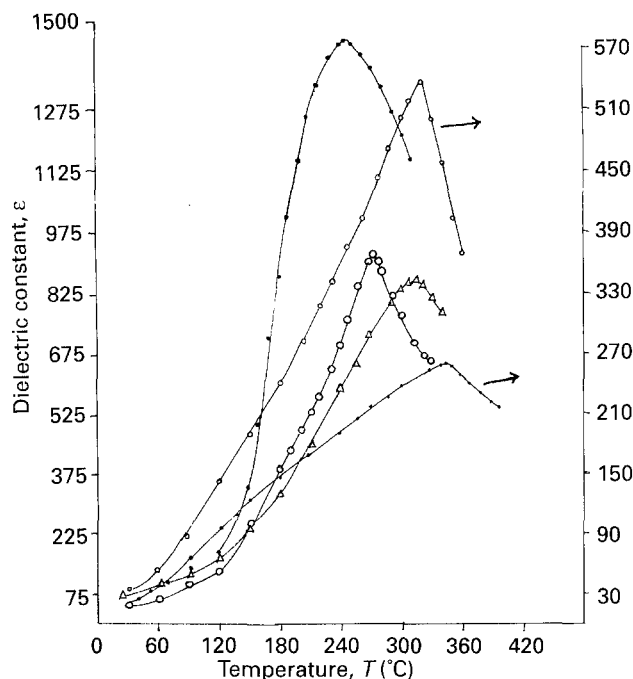


Figure 1 Dielectric constant versus temperature diagram for La-SCN:  $(\text{Sr}_{1-x}\text{La}_{2x/3})(\text{Cu}_{1/3}\text{Nb}_{2/3})\text{O}_3$ ,  $x = (\bullet) 0, (\circ) 0.075, (\triangle) 0.150, (\odot) 0.225$  and  $(\blacktriangle) 0.300$ .

do not coincide with the corresponding Curie temperatures. Such anomalous behaviour has been reported previously for samples containing perovskite-type oxygen octahedra [9, 10]. The resistivity maxima at a certain temperature is one of the properties of semiconductor materials. In La-SCN samples the introduction of La into the SCN lattice does not seem to change this behaviour. This means that substitution of La has no effect on the energy band structure of the SCN lattice. Trivalent dopants in  $\text{BaTiO}_3$  raise an interesting situation, as they can behave as donors or as acceptors, depending on the site occupied [11]. However, aliovalent dopants in SCN substitute only for  $\text{Sr}^{2+}$  because of their ionic radii [12] ( $\text{Sr}^{2+}$  0.154 nm,  $\text{La}^{3+}$  0.146 nm,  $\text{Cu}^{2+}$  0.087 nm and  $\text{Nb}^{5+}$  0.078 nm) and hence act as donors. Since conduction is a thermally activated process, conductivity ( $\sigma$ ) can be expressed as  $\sigma = \sigma_0 \exp(-E_a/kT)$ , where  $\sigma_0$  is a constant,  $E_a$  is the activation energy for conduction,  $k$  is the Boltzmann constant and  $T$  is the absolute temperature. The slope of the Arrhenius plot of  $\ln \sigma$  and  $1/T$  therefore corresponds to  $-E_a/k$ , from which the activation energy for conduction may be obtained. The activation energies so computed and the resistivity at room temperature ( $\rho_{\text{RT}}$ ), at peak

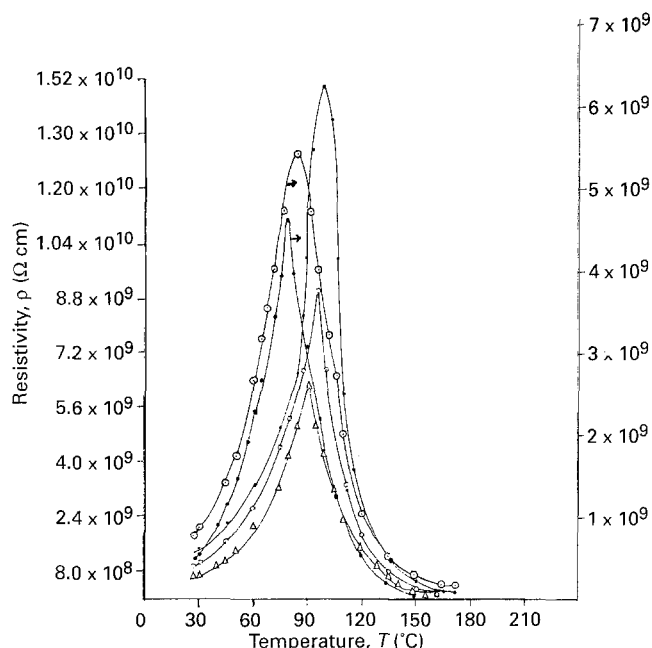


Figure 2 D.c. resistivity versus temperature diagram for La-SCN:  $(\text{Sr}_{1-x}\text{La}_{2x/3})(\text{Cu}_{1/3}\text{Nb}_{2/3})\text{O}_3$ ,  $x = (\bullet) 0, (\circ) 0.075, (\triangle) 0.150, (\odot) 0.225$  and  $(\blacktriangle) 0.300$ .

temperature ( $\rho_{\text{Tc}}$ ) and corresponding temperature ( $\rho_{\text{T}}$ ) are given in Table II.

In view of the above observations, it is concluded that the system  $(\text{Sr}_{1-x}\text{La}_{2x/3})(\text{Cu}_{1/3}\text{Nb}_{2/3})\text{O}_3$  is monophasic and tetragonal for all values of  $x$  ranging from 0.0 to 0.30. Progressive addition of lanthanum causes a lowering in  $T_c$  and manifests significant change in the conductivity properties.

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TABLE II Curie point, dielectric constant, resistivity and activation energy data for the samples

Sample	$T_c$ (°C)	$\epsilon_{\text{RT}}$	$\epsilon_{\text{TC}}$	$C(\times 10^5)$	$\rho_{\text{RT}} (\times 10^8 \Omega \text{ cm})$	$\rho_{\text{TC}} (\times 10^9 \Omega \text{ cm})$	$\rho_{\text{T}} (\text{°C})$	$E_a$	
								+ve	-ve
$\text{Sr}(\text{Cu}_{1/3}\text{Nb}_{2/3})\text{O}_3$	345	24	255	0.7	3.53	14.9	100	0.25	0.11
$\text{Sr}_{0.925}\text{La}_{0.05}(\text{Cu}_{1/3}\text{Nb}_{2/3})\text{O}_3$	320	34	537	0.4	9.43	8.8	95	0.28	0.13
$\text{Sr}_{0.850}\text{La}_{0.10}(\text{Cu}_{1/3}\text{Nb}_{2/3})\text{O}_3$	307	62	853	2.2	6.71	6.2	90	0.25	0.14
$\text{Sr}_{0.775}\text{La}_{0.15}(\text{Cu}_{1/3}\text{Nb}_{2/3})\text{O}_3$	272	51	919	1.1	7.18	5.3	85	0.26	0.15
$\text{Sr}_{0.700}\text{La}_{0.20}(\text{Cu}_{1/3}\text{Nb}_{2/3})\text{O}_3$	245	68	1439	3.0	4.83	4.5	77.5	0.25	0.13

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