

## Electrical conduction in the system $\text{Sr}_{0.90}\text{La}_{0.10}\text{Ti}_{0.90}\text{M}'_{0.10}\text{O}_3$ ( $\text{M}' = \text{Co}, \text{Ni}$ or $\text{Cr}$ )

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MS received 24 June 1996

**Abstract.** We have successfully synthesized the system  $\text{Sr}_{1-x}\text{La}_x\text{Ti}_{1-x}\text{M}'_x\text{O}_3$  where  $\text{M}' = \text{Cr}, \text{Ni}$  and  $\text{Co}$  by using conventional solid state ceramic method. Powder X-ray diffraction patterns of the different compositions show the formation of single phase materials. Measurement of AC conductivity as a function of frequency at different temperatures in the range 300–550 K show that conduction in these compositions occurs due to hopping of charge carriers between localized transition metal ion sites.

**Keywords.** Perovskite; substitutions; hopping conduction.

### 1. Introduction

Alkaline earth titanates exhibit interesting dielectric properties with high resistivity and are useful in electronic applications. In this class of materials, properties are governed by distortion in lattice i.e. change in lattice parameters and symmetry. In case of oxides of transition metal ions with lanthanum, electrical properties are governed by the valence state and the spin state of the transition metal ions. The properties of these materials can further be modified and exploited for technical applications by compositional modifications and by changing different processing parameters (Buchanan 1986). For the last few years, we are studying the dielectric and electrical properties of valence compensated solid solutions of these oxides. For the system  $\text{M}_{1-x}\text{La}_x\text{Ti}_{1-x}\text{Co}_x\text{O}_3$  ( $\text{M} = \text{Pb}, \text{Ba}, \text{Sr}$  and  $\text{Ca}$ ), studies on electrical behaviour show that conductivity continuously increases with increase in  $x$ . Since other ions have inert gas configuration, it is concluded that cobalt ions in these systems play an important role in electrical conduction behaviour (Parkash *et al* 1987, 1989a, b, 1990). In order to study the effect of transition metal ions on electrical properties of valence compensated perovskite oxides, a typical composition with different transition metal ions  $\text{Sr}_{0.90}\text{La}_{0.10}\text{Ti}_{0.90}\text{M}'_{0.10}\text{O}_3$  ( $\text{M}' = \text{Co}, \text{Ni}$  and  $\text{Cr}$ ) prepared under identical conditions, was studied. This represents the solid solutions between  $\text{SrTiO}_3$  and  $\text{LaCoO}_3$ ,  $\text{LaNiO}_3$  or  $\text{LaCrO}_3$ .

### 2. Experimental

The investigated samples were prepared by conventional solid state ceramic method by mixing appropriate quantities of strontium carbonate, titanium dioxide, lanthanum oxalate, cobalt oxalate, basic nickel carbonate and chromium oxide, all having purity better than 99.5% in an agate mortar using acetone as a grinding medium. The mixed,

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**Table 1.** Values of lattice parameter,  $a$  (Å), activation energies,  $E_a$  and  $E_b$  (eV) and hopping energy,  $W_H$  (eV) for different compositions in the system,  $\text{Sr}_{0.90}\text{La}_{0.10}\text{Ti}_{0.90}\text{M}'_{0.10}\text{O}_3$  ( $\text{M}' = \text{Co}, \text{Ni}$  and  $\text{Cr}$ ).

M'	Lattice parameter $a$ (Å)	Activation energy		Hopping energy $W_H$ (eV)
		$E_a$ (eV)	$E_b$ (eV)	
Co	3.875	0.39	0.56	0.18
Ni	3.888	0.21	0.54	0.32
Cr	3.892	0.18	0.43	0.25

dried powders were calcined at 1523 K. The calcined and reground powders were pelletized in the form of cylindrical pellets. These pellets were sintered at 1673 K for 12 h and then furnace cooled. X-ray diffraction patterns of the final products were taken in a X-ray diffractometer using  $\text{Cu K}_\alpha$  radiation. For conductivity measurements, polished pellets were coated with silver paint cured at 900 K for 30 min. Conductance ( $G = 1/R$ ) was measured as a function of temperature and frequency using Hewlett Packard impedance analyser, HP 4192A LF.

### 3. Results and discussion

Powder X-ray diffraction data of the samples show the formation of single phase material. XRD patterns did not contain any line characteristic of the constituent oxides or any other compound among them. XRD data could be indexed on the basis of a cubic unit cell similar to strontium titanate and calculated lattice parameter 'a' is given in table 1. It is noted from the table that the lattice parameter is highest for Cr substituted samples and lowest for Co substituted samples. This can be understood in terms of decreasing ionic radii of the substituents {La(1.32 Å), Co(0.525 Å), Ni(0.56 Å), Cr(0.615 Å)} in comparison to ions going to be substituted {Sr(1.44 Å), Ti(0.605 Å)} (Shannon and Prewitt 1970).

For all the samples, the variation of  $\log \sigma_{AC}$  as a function of  $\log f$  at two different temperatures is shown in figure 1 for all the samples at two different temperatures. It is observed that AC conductivity increases with increase in frequency. Variation of  $\log \sigma_{AC}$  with  $\log f$  obeys the relation (Austin and Mott 1969):

$$\text{Log } \sigma_{AC} = A\omega^s,$$

where  $A$  is constant at particular temperature and  $s$  a weak function of frequency. In these plots, two regions are observed. A low frequency region where frequency dependence of  $\log$  of AC conductivity is less in comparison to higher frequency region. At higher temperatures, frequency dependence of AC conductivity decreases i.e. the value of  $s$  decreases. A variation of logarithm of DC resistivity with inverse of temperature for these samples is shown in figure 2 where DC resistivity was calculated from the slopes of the  $V-I$  plots of these samples at different temperatures. Figure 3 shows the variation of  $\log$  of AC conductivity with  $1000/T$  at 100 KHz for Co, Ni and Cr substituted samples. In both figures 2 and 3, two regions are observed. A lower temperature region having low value of activation energy and a higher temperature

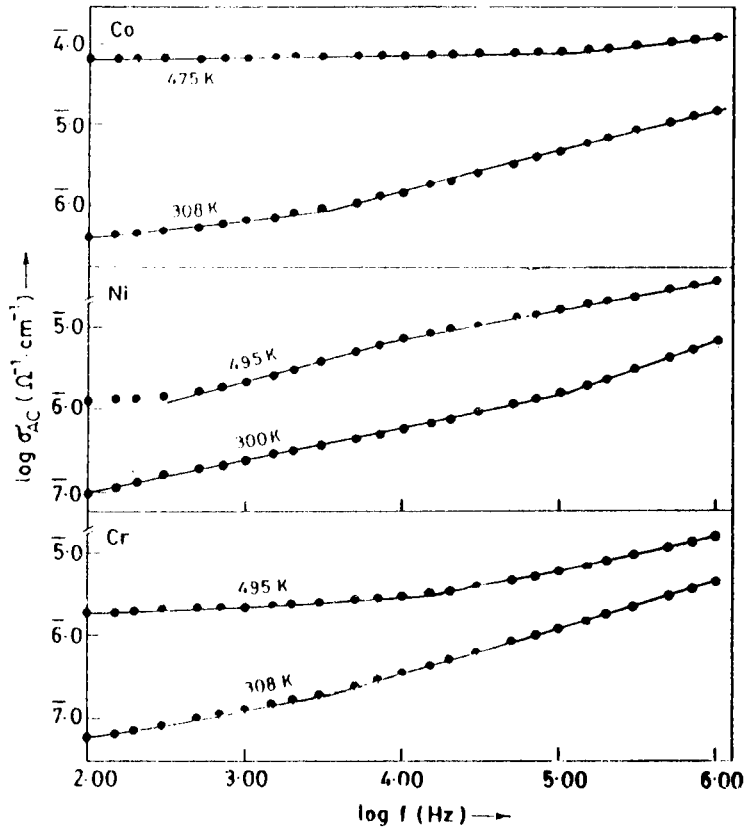


Figure 1. Variation of  $\log \sigma_{AC}$  as a function of frequency at two different temperatures.

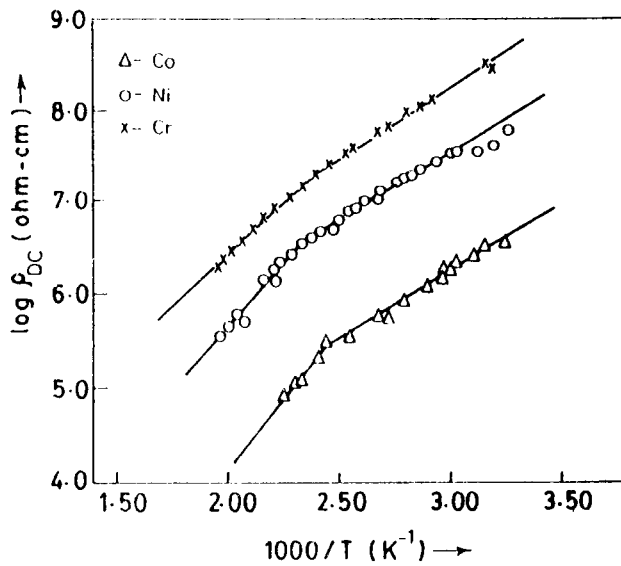


Figure 2. Plots of  $\log \rho_{DC}$  against inverse of temperature.

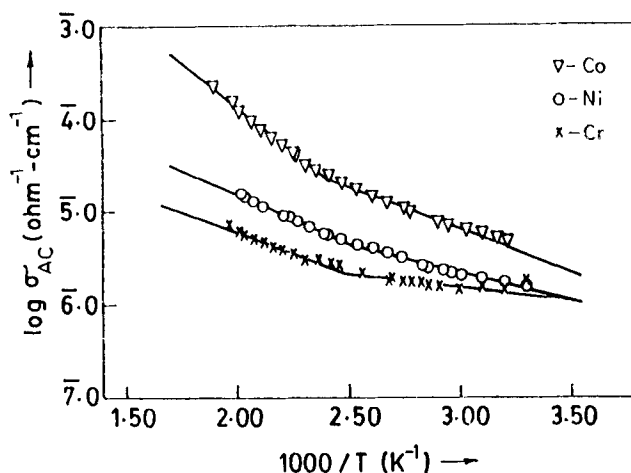


Figure 3. Variation of  $\log \sigma_{AC}$  as a function of inverse of temperatures for different compositions.

region where dependence of AC conductivity on temperature is more pronounced. Activation energies calculated from these plots using least square fit of the data are given in table 1 for both temperature regions.

For these compositions, the conduction process is predominantly due to the 3d electrons of the transition metal ions as already reported (Parkash *et al* 1993a, b). In lower temperature region, the conductivity may be due to hopping of charge carriers among localized sites (Pollak and Gaballe 1961; Austin and Mott 1969) giving rise to a frequency dependence of AC conductivity as  $\omega^s$  and little temperature dependence. At higher temperatures, the conduction occurs by transport of charge carriers excited into localized states at the valence band edge and hopping at energies close to it. The frequency and temperature dependence of conductivity in such a case is given by (Elliot 1978)

$$\sigma_{AC}(\omega, T) = (\pi/96)^3 e^2 \alpha^{-5} \cdot kT [N(E_A)]^2 \omega [\ln(v_{ph}/\omega)]^4 \exp[-(E_F - E_A)/kT].$$

The variation of DC resistivity for this mechanism is given by

$$\rho = \rho_0 \exp\{(E_F - E_A - W_H)/kT\},$$

where  $E_A$  represents the valence band edge and  $W_H$  the activation energy for hopping. For this mechanism both AC and DC conductivity vary exponentially with temperature. However, the activation energies for AC and DC conduction are different. The difference between these two values gives the value of activation for hopping. The value of hopping energy ( $W_H$ ) for these compositions are given in table 1. Same conduction mechanism is operative in similar systems already reported (Parkash *et al* 1993a, b).

In this system, conductivity increases from Cr substituted composition to Co substituted composition. In these samples, transition metal ions of different valencies are present. Presence of these multivalent ions can be understood as follows. When these materials are sintered at high temperature, they lose traces of oxygen during sintering and in this process extra electrons are released. These electrons are captured by transition metal ions and produce small amounts of ions of different valency. These

ions which are on Ti<sup>4+</sup> sites form dipole with positively charged oxygen vacancies V<sub>O</sub><sup>••</sup>. These dipoles can change their orientation by hopping of electrons among these transition metal ions of different valencies. As the radii of transition metal ions decreases, change in orientation of dipoles (hopping of electrons) become easy due to change in polarizability. For charge transport in these samples, transition metal ion and oxygen vacancy distance is important. As the ionic radii of transition metal ion decreases, the transition metal ion–oxygen vacancy distance increases which facilitate the hopping of charge carriers (George and Grace 1969). In transition metal ions, the ability of ions to change the valency in different environment also decreases from Co to Cr ions. Measurement of magnetic susceptibility of Cr, Ni and Co doped BaTiO<sub>3</sub> compositions also show the increasing trend from Cr substituted samples to Co substituted compositions (Ihrig 1978).

### Acknowledgements

Authors are thankful to the All India Council for Technical Education, New Delhi for financial assistance and one of us (HST) is very much thankful to Prof. V B Tare and Dr Om Parkash, Department of Metallurgical Engineering, Banaras Hindu University, Varanasi for facilities.

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