Structural studies of LaSrNiO$_4$, LaSrNi$_{0.7}$Fe$_{0.3}$O$_4$ and LaSrNi$_{0.7}$Co$_{0.3}$O$_4$

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The compounds LaSrNiO$_4$, LaSrNi$_{0.7}$Fe$_{0.3}$O$_4$ and LaSrNi$_{0.7}$Co$_{0.3}$O$_4$ have been prepared by ceramic method. The powder X-ray diffraction studies show that these phases crystallize in tetragonal unit cell with I4/mmm space group. Electric transport study suggests that electrical conduction follows Mott type three dimensional variable range hopping mechanism and the characteristic energy of hopping increases manifold with partial substitution of cobalt and iron ions. Magnetic studies suggest that doping causes appreciable changes in magnetic susceptibility.

A number of Ruddlesden-Popper type phases of the composition Ln$_{n}$Sr$_{m}$M$_{n+1}$O$_{3n+1}$ (Ln = rare earth ion and M = transition metal ion) are known$^1$-$^4$. In this class of materials, LaSrNiO$_4$ and some of its substituted analogues are reported in literature$^5$-$^8$. However, there are conflicting reports of electric transport properties of LaSrNiO$_4$. Some studies show that the data follow Arrhenius type conduction mechanism$^6$, while another study suggests that variable range hopping mechanism governs the electrical conduction$^2$. It was thought of interest to study the physical properties of LaSrNiO$_4$, as functions of temperature, and investigate the effect of partial replacement of nickel by iron and cobalt on the properties.

Experimental
The oxides viz. La$_2$O$_3$, SrO, NiO, Fe$_2$O$_3$ and Co$_3$O$_4$ used in this study were of AR grade and used as such.

The reactant oxides were weighed in proper ratios, corresponding to the stoichiometry of the desired phases, homogenized by grinding and mixing and pressed into pellets. The pellets were heat-treated at 1323 K in continuous flow of dry oxygen for at least 48 h with a number of intermediate grindings and pelletizing. Room temperature powder X-ray diffraction data of the samples were recorded on a Philips Diffractometer type PW 1050/71 at a scanning speed of 1°/min using CuK$_\alpha$ radiations. The total amount of various constituent cations was determined by the usual chemical means$^9$. Oxygen stoichiometry was determined by iodometric titration$^{10}$ and the titrable oxygen content, within the error limits of ±0.03, corresponded to the stoichiometry of different phases given in Table 1. Electrical resistivity of the sintered pellets of these phases was recorded by four probe method using a Leybold closed cycle helium cryostat and Keithley constant current source 224 and nanovoltmeter 181. Thin copper wires were attached to the surface of pellets with silver paste for the purpose of electrodes. Magnetic susceptibility of the polycrystalline materials was measured by Faraday technique in the temperature range 77-300 K using Hg[Co(SCN)$_4$] as calibrant in an external magnetic field of 3,700 gauss. All magnetic susceptibility values were corrected for diamagnetism of the constituent ions.

Results and discussion
The X-ray diffraction data of LaSrNiO$_4$, LaSrNi$_{0.7}$Fe$_{0.3}$O$_4$ and LaSrNi$_{0.7}$Co$_{0.3}$O$_4$ could be indexed for tetragonal unit cell and the cell parameters so calculated were refined by the computer programme ‘Cell’. The refined parameters are given in Table 1. The data suggest that c increases appreciably with the substitution while there is minor change in a. The theoretical diffraction data for these phases were generated from the computer programme ‘Lazy-Pulverix’ on the basis of space group I4/mmm. There is good agreement between the experimental and theoretical intensities considering that any preferred orientation effects are neglected, which suggests that the phases crystallize in this space group.

Various equations based upon different mechanisms of conduction, such as those applicable in case of Arrhenius model, polaron hopping model and variable range hopping model have been applied to the data of electrical resistivity for LaSrNiO$_4$, LaSrNi$_{0.7}$Fe$_{0.3}$O$_4$ and LaSrNi$_{0.7}$Co$_{0.3}$O$_4$. It was observed that the equation based on three dimensional variable range hopping mechanisms, \( \rho = \rho_0 \exp(B/T^4) \), was applicable to the data. \( \log \rho \) versus \( T^{-4} \) plots are linear. The linearity of plots suggests that Mott’s three dimensional variable range hopping mechanism governs the electrical conduction as observed by Sreedhar and Honig$^5$. The characteristic energy of hopping (B) has been computed...
from the log $\rho$ versus $T^{-1}$ plots. The values are given in Table 1. The increase in characteristic energy of hopping (B) with partial substitution of iron and cobalt in nickel suggests that insulating behaviour increases with doping and it is more pronounced in case of iron compound than that associated with the cobalt containing phase.

Plots of $X_M^{-1}$ versus $T$ show that magnetic susceptibility of LaSrNiO$_4$ changes only slightly in the temperature region of the present study. However, partial substitution at nickel site results in appreciable variation in magnetic susceptibility with change in temperature. The paramagnetic Curie temperature ($\theta$) in the doped phases, prepared by partial replacement of Ni$^{3+}$ by Fe$^{3+}$ or Co$^{3+}$ ions, has negative values. The magnetic moments for these phases have been calculated from the slopes of plots and these values along with $\theta$ are given in Table 1. The theoretical magnetic moments have been calculated from the following additive law:

$$\mu_{\text{cal}} = X_M \mu_\text{M} + X_S \mu_\text{S},$$

where $\mu$ are the theoretical magnetic moments and $X$ are the molar fractions of the parent and the substituted ions respectively. The calculated magnetic moments are also given in Table 1.

A comparison of calculated and experimental magnetic moments suggest that Ni$^{3+}$ ions in all these phases are in low spin states ($t^6_{2g} e^1_g$), while Fe$^{3+}$ ion in LaSrNiFe and Co$^{3+}$ ion in LaSrNiCoO$_4$ are in their high spin states ($t^2_{2g} e^2_{g}$) and ($t^1_{2g} e^2_{g}$) respectively. As a result of antiferromagnetic interactions, the observed values are comparatively lower than the theoretical values.

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References
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