SUMMARY
Some new manganites of the general formula \( \text{ZnMn}_{2-x}\text{Ni}_x\text{O}_4 \) have been synthesized and their structural, electrical and magnetic properties have been studied.

These compounds were prepared by grinding mixtures of \( \text{ZnO}, \text{MnO}_2 \) and \( \text{NiO} \) in appropriate proportions in alcohol, followed by reaction in oxygen atmosphere at \( 900^\circ\text{C} \pm 10^\circ\text{C} \) for about five hours. The resultant product was reground and reacted again at \( 1100^\circ\text{C} \pm 10^\circ\text{C} \) in oxygen atmosphere for 3 hours.

X-ray powder diffraction patterns showed that no unreacted oxides were present. On the basis of the charge neutrality conditions, it was concluded that incorporation of the \( \text{Ni}^{2+} \) ions changed the valence state of \( \text{Mn}^{3+} \) ions to \( \text{Mn}^{4+} \) ions. The general formula of the compound would therefore be \( \text{Zn}^{2+}[\text{Ni}^{2+}\text{Mn}_{2-2x}^{3+}\text{Mn}_x^{4+}]_0\text{O}_4 \).

The crystal structure of these compounds was determined by the x-ray powder diffraction methods and the unit cell values were determined by the method of successive refinements. The cation distribution was inferred from the well-known site preference energies of these ions in the spinel structure and it was concluded that the \( \text{Zn}^{2+} \) ions occupy the tetrahedral sites and \( \text{Ni}^{2+}, \text{Mn}^{3+}, \text{Mn}^{4+} \), ions the octahedral sites. This cation distribution is consistent with the observed crystal structure of the compound.
The compounds prepared as described above were ground and pressed into pellets with an appropriate binder. The pellets were then sintered at about 1150° ± 10°C in O₂ atmosphere and the electrical properties of these pellets were measured as a function of temperature. The change of electrical conductivity with temperature follows the well known relationship:

$$\sigma = \sigma_0 \exp \left(-\frac{\Delta E}{kT}\right)$$

$\Delta E$ the energy of activation being dependent on the composition (Table No.10).

The thermoelectric coefficient measurements indicate that the compounds in which $[\text{Mn}^{4+}] < [\text{Mn}^{3+}]$ $(0 < x < 0.5)$ are p-type semiconductors while those in which $[\text{Mn}^{3+}] < [\text{Mn}^{4+}]$ are n-type semiconductors. The only inconsistency is observed in the composition $2\text{MnNi}_{0.5}\text{Mn}_{1.5}O_4$ where $\text{Mn}^{4+} < \text{Mn}^{3+}$ and hence the compound should be p-type but is actually observed to be n-type. This is explained on the basis of the fact that thermoelectric coefficient is given by the formula:

$$S = \frac{A}{eT} + \frac{K}{e} \ln \frac{[\text{Mn}^{3+}]}{[\text{Mn}^{4+}]}$$

where $e$ is the electronic charge. The term $A$ represents the kinetic energy transported by the migrating electrons. Usually the second term predominates and determines the sign of $S$. But when $[\text{Mn}^{3+}] \approx [\text{Mn}^{4+}]$ then the second term becomes very small and the sign of $S$ is determined by the sign of $A$. 
The calculated mobility values show that the charge carriers are localized and the electrical conduction is due to the hopping of the charge carriers from one Mn$^{3+}$ ion to the adjacent Mn$^{4+}$ ion at the octahedral site.

Paramagnetic susceptibility of these compounds has been measured by the Gouy method in the temperature range 100°K to about 340°K. All the compounds showed a pronounced decrease in $1/\chi$ vs T curve below 110°K, similar to ferrimagnetic compounds. Such a behaviour can also be attributed to be due to the presence of clusters of ferromagnetically ordered ions in our compounds, leading to super-paramagnetic phenomenon.

Electrical properties of thin films of manganites of following compositions were studied:

Cu$_{1.5}$Mn$_{1.5}$O$_4$, CuMn$_2$O$_4$, Cu$_{0.75}$Ni$_{2.25}$O$_4$, Ni$_{0.9}$Cu$_{0.1}$Mn$_2$O$_4$ and CoMn$_2$O$_4$. The change of electrical conductivity with temperature in these thin films was also found to follow the relationship:

$$\sigma = \sigma_0 \exp(-\Delta E/kT)$$

$\Delta E$ being dependent upon the composition. In case of copper manganite samples a sharp change in the energy of activation for electrical conduction was observed at high temperatures. This is attributed to be due to the change in the valence state of copper ions at high temperatures. The effect of the atmosphere (air, O$_2$ and N$_2$) on the conductivity of some of these films was also studied, but no appreciable change in the conductivity due to the change of atmosphere was observed.