

# ABSTRACT

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Thorough investigations regarding the effects of Ni doping on Fe site in LaFeO<sub>3</sub> on the structural, electronic, ac electrical, dielectric and magnetic properties has been performed using synchrotron X-ray diffraction, X-ray absorption, dc magnetization, Mossbauer and impedance spectroscopy. Polycrystalline LaFe<sub>1-x</sub>Ni<sub>x</sub>O<sub>3</sub> (x = 0.0, 0.1, 0.3 & 0.5) oxides were prepared by the solid state reactions method. The results and brief relevant theoretical introduction of each experimental technique are presented and discussed in a separate chapter. Chapter 1 encircles brief description of the importance of LaFe<sub>1-x</sub>Ni<sub>x</sub>O<sub>3</sub>, importance of the experimental techniques used for these characterizations, motivations and objectives of the present study. The synthesized samples are the orthorhombically distorted derivatives of an ideal perovskite structure. Anomalous variations in the perovskite distortions have been observed and attributed to the energy effects associated with partial filling of the degenerate orbitals and the hybridization of the localized orbitals at cations and anions, invoked by Ni doping in LaFeO<sub>3</sub>. To investigate the effects of Ni doping on the oxidation state, spin state and magnetic ordering of Fe cations in LaFeO<sub>3</sub>, <sup>57</sup>Fe Mossbauer experiment (at room temperature) and dc magnetization measurements between 4K and 400K have been performed. The iron is present in high spin 3+ and 4+ oxidation states. Density of Fe<sub>4+</sub> increases with Ni doping. Fe<sub>3+</sub> cations in LaFeO<sub>3</sub> are antiferromagnetically ordered. The weak ferromagnetic component in M-H curves is due to the canted spin structure of Fe cations in LaFeO<sub>3</sub>. Temperature independence of the saturation magnetization associated with this weak ferromagnetic component strongly suggests that the degree of spin canting is invariant with between 4K and 400K. A progressive collapse of the magnetically ordered state of Fe in LaFeO<sub>3</sub> to a spin disordered state on Ni doping has been observed and discussed in terms of increase in the spin relaxation frequency and dilution of the Fe<sub>3+</sub> sublattice (five unpaired spins: t<sub>2g</sub><sup>3</sup>, e<sub>g</sub><sup>2</sup>) by Fe<sub>4+</sub> (four unpaired spins: t<sub>2g</sub><sup>3</sup>, e<sub>g</sub><sup>1</sup>) and low spin Ni<sub>2+</sub>/Ni<sub>3+</sub> cations. The possibility of any transition of the Fe<sub>3+</sub> from the high spin state to low spin state and hence its role to mediate this collapse in the magnetically ordered state has been totally excluded. Analysis of the Fe K-edge X-ray absorption spectra in the XANES and EXAFS regions confirmed the results of Mossbauer spectroscopy and XRD regarding oxidation state of Fe and octahedral deformations, respectively. Ni is found as Ni<sub>3+</sub> in LaFe<sub>0.9</sub>Ni<sub>0.1</sub>O<sub>3</sub> and the density of Ni<sub>2+</sub> increases with further Ni doping. Temperature dependence of the position and strength of the ac electrical relaxations indicates that the electrical conduction and dielectric polarization in LaFe<sub>1-x</sub>Ni<sub>x</sub>O<sub>3</sub> are due to the small polaronic hopping of the holes state between Fe<sub>4+</sub> and Fe<sub>3+</sub>. The observed colossal value of the dielectric constant in LaFeO<sub>3</sub> is an extrinsic effect and its origin lies in the extended defects at grain-grain and sample-electrode interfaces. Variations in the resistance and the capacitance associated with grain and grain boundaries has been conferred in terms of the density of the electrical charge carriers, potential barriers height at grain boundaries and thickness of the grain boundaries. O K-edge XANES spectra shows the growth of two new important conduction bands with doping Ni in LaFeO<sub>3</sub>. One is the localized

conduction band „L“, associated with the holes states introduced at the iron cations. The other band „m“ is of itinerant nature and is due to the hybridization of O2p states with Ni3d states. From the increase in spectral intensity of „L“ or the concentration of Fe<sup>4+</sup> (hopping channel for the localized conduction), a progressive increase in the mobility and decrease in the activation energy for hopping of the localized electrical charge carriers was expected and observed. From the simultaneous growth of both of these bands, a competition between these two parallel conduction in LaFe<sub>1-x</sub>Ni<sub>x</sub>O<sub>3</sub> can be predicted. Dominancy of either the itinerant or localized type conduction in any composition of LaFe<sub>1-x</sub>Ni<sub>x</sub>O<sub>3</sub> is determined by the dominancy of these conduction bands. Metallic character in LaFe<sub>1-x</sub>Ni<sub>x</sub>O<sub>3</sub> increased progressively with increasing Ni. This again was in accordance to the growing intensity of the delocalized conduction band „m“. Although, the activation energy for hopping of holes between Fe<sup>4+</sup> and Fe<sup>3+</sup> decreased with the increase in Ni doping, however, localized type conductivity associated with the iron lattice remained non-zero even in half doped sample „LaFe<sub>0.5</sub>Ni<sub>0.5</sub>O<sub>3</sub>“. It indicated that the holes introduced into the iron cations were localized and the itinerant behavior of the electrical charge carriers associated with the iron cations have not completely established. The composition dependent metal to insulator transition in LaFe<sub>1-x</sub>Ni<sub>x</sub>O<sub>3</sub> is associated dominantly with the metallic character at the Ni sites rather than the new holes state at the Fe cations.