Effect of LaNiO$_3$ on the impedance and dielectric properties of CoFe$_2$O$_4$: a high temperature study: Supplementary material

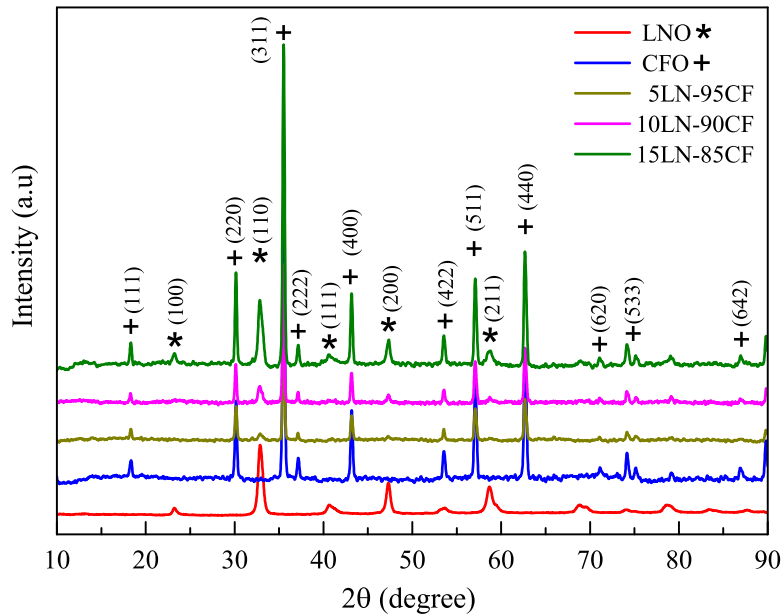**Ananya Patra**[1,*] **and V Prasad**[1]

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1. X-ray diffraction

Figure 1. XRD pattern of the composites xLNO + (1-x)CFO where x = 0, 0.5, 0.10, 0.15, 0.20 and 1

Figure 1 shows the X-ray diffraction pattern of the series [xLNO +(1-x)CFO (x = 0, 0.05, 0.10, 0.15, 0.20 and 1)] which confirms the phase formation of the two materials LNO and CFO and the phase purity of their composites. The independent presence of the peaks of LNO and CFO (indicated by * and + respectively) reveals

that both materials co-exist in the composites. Although the CFO peaks are more prominent than LNO because of higher percentage of CFO. The diffraction peaks of CFO correspond to cubic spinel structure with space group Fd$\bar{3}$m (JCPDS No. 22-1086). Since there is no peak splitting of LNO in pure form and also in the composites, the peaks of LNO are indexed by the cubic perovskite structure with space group Pm$\bar{3}$m (JCPDS No. 33-0710). We calculated the crystallite size of LNO and CFO using Scherrer equation. The variation of average crystallite size of LNO in pure form and in composites is from 14 nm to 19 nm and that of CFO is from 34 nm to 38 nm. The lattice parameters (a) of pure LNO and CFO as obtained from the relation: $a = d_{hkl}\sqrt{h^2 + k^2 + l^2}$ are 3.846 Åand 8.371 Årespectively, where d_{hkl} is the lattice spacing and (h,k,l) are the Miller indices. The lattice parameter shows negligible change in the composites.
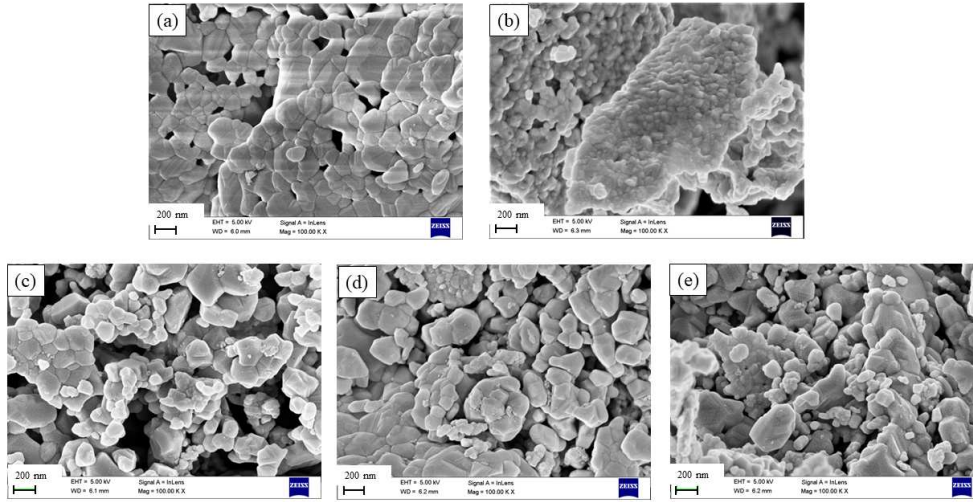

Figure 2. SEM images of (a) pure CFO, (b) pure LNO and the composites: (c) 5LN-95CF, (d) 10LN-90CF and (e) 15LN-85CF.

2. SEM

The morphologies of pure and composite materials [xLNO +(1-x)CFO (x = 0, 0.05, 0.10, 0.15, 0.20 and 1)] are investigated by scanning electron microscopy as presented in Figure 2. The samples are formed of grains separated by grain boundaries which is also evident from the result of impedance spectroscopy as discussed in the main manuscript. As it depicts from the figure, the grain size of pure CFO is little bit higher than pure LNO. Hence the small grains in the composites belong to LNO and the large grains are formed by CFO.

3. Magnetic property

To investigate the magnetic properties, we have obtained the hysteresis loop (magnetization (M) vs. magnetic field ($\mu_0 H$)) at room temperature for different
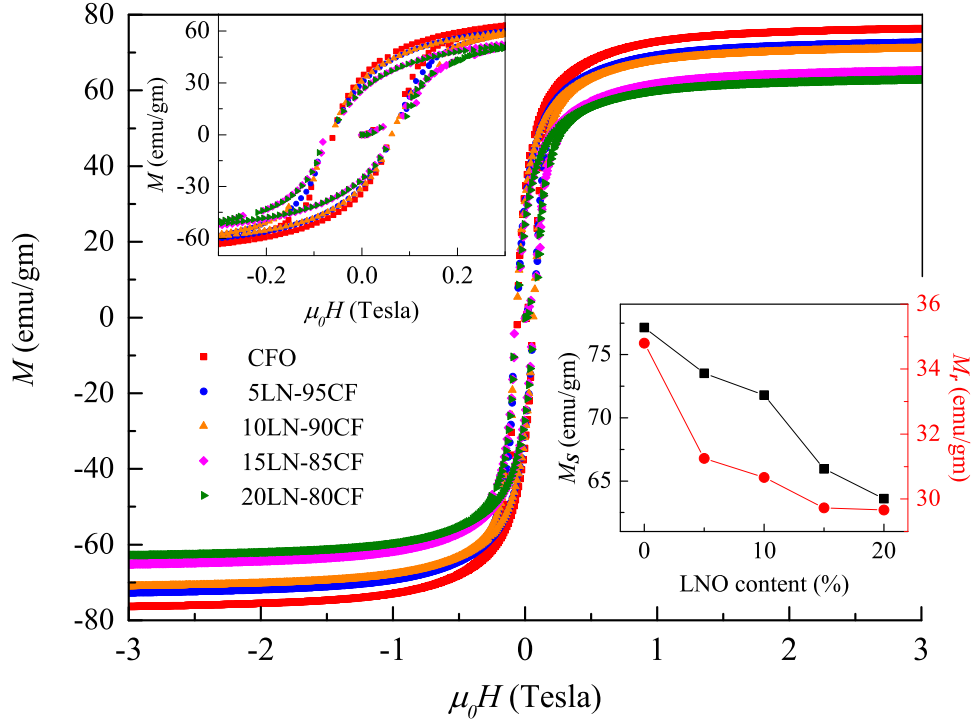
Figure 3. Magnetization as a function of magentic field at room tempeature (300 K) of pure CFO and the composites with LNO content 5, 10 and 15 %. Top inset shows the enlarge view at low magentic field and the bottom inset depicts the variation of satuaration and remenant magnetization with LNO content.

composites [xLNO +(1-x)CFO (x = 0, 0.05, 0.10, 0.15, 0.20)] as shown in Figure 3. The top inset represents the enlarge view at low magnetic field which shows there is not much variation in the coercivity for different composites. However, the values of saturation (M_S) and remanent magnetization (M_r) are reduced consistently with decreasing CFO content as shown in the bottom inset of Figure 3.

4. Dielectric properties of 15LN-85CF

The real part of the dielectric constant for the composite 15LN-85CF is plotted in log-log scale in Figure 4 to clearly visualize the relaxation behaviour. Two strong relaxations are observed at different frequency range, the grain boundary one at 35–200 °C and the electrode polarization appears at $\geq$ 100 °C at comparatively lower frequency. Both relaxations shift to high frequency side with raising temperature which is also consistent with the impedance spectroscopy measurement. As we have observed from the impedance and modulus spectroscopy of the composite 15LN-85CF, the grain is more conductive and less capacitive, hence the grain relaxation behaviour
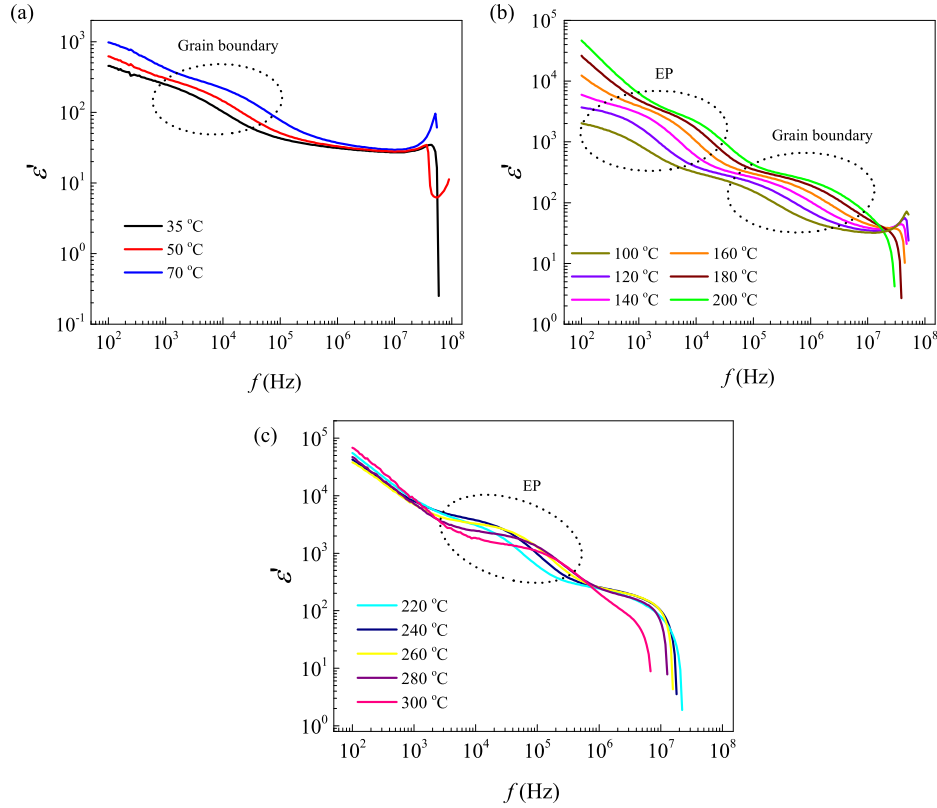
Figure 4. Real part of the dielectric constant plotted in log-log scale for the composite 15LN-85CF at different temperature showing (a) the grain boundary relaxation at 35–70 °C, (b) the relaxation of both grain boundary and electrode polarization (EP) at 100–200 °C and (c) EP at 220–300 °C.

is not prominent. Therefore, the contribution to the dielectric constant mostly comes from the orientation and interfacial polarization of the trapped charge carriers at the grain boundaries or at the electrode-surface interfaces. At temperature below 100 °C, the polarization effect comes from grain boundary charge carriers, at the intermediate temperature (100–200 °C) both grain boundary and electrode polarization take place and at high temperature (> 200 °C) when the trapped charges can hop across the grain boundary due to thermal activation, the majority of the contribution comes from electrode polarization.