Study of structural and dielectric properties of $\text{La}_{0.9}\text{Na}_{0.1}\text{CrO}_3$ - and $\text{Ni}_{0.5}\text{Cu}_{0.5}\text{Fe}_2\text{O}_4$ -based composites

M. Saleem*, Shivani Chouhan and A. Mishra
Materials Science Laboratory, School of Physics
Vigyan Bhawan, Devi Ahilya University
Khandwa Road Campus, Indore 452001, India
*tabindat2014@gmail.com

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The preparation of $\text{La}_{0.9}\text{Na}_{0.1}\text{CrO}_3$ (LNCO), $\text{Ni}_{0.5}\text{Cu}_{0.5}\text{Fe}_2\text{O}_4$ (NCFO) and their composites of the type $(1-x)\text{La}_{0.9}\text{Na}_{0.1}\text{CrO}_3$ (LNCO) + $(x)\text{Ni}_{0.5}\text{Cu}_{0.5}\text{Fe}_2\text{O}_4$ (NCFO) ($x = 0.25, 0.50$) through solid state route is reported. From X-ray diffraction data analysis, the parent $\text{La}_{0.9}\text{Na}_{0.1}\text{CrO}_3$ was found to crystallize in orthorhombic structure ($Pnma$) while $\text{Ni}_{0.5}\text{Cu}_{0.5}\text{Fe}_2\text{O}_4$ has crystallized into the cubic structure ($Fd3m$) further verified via Rietveld refinement. The morphology and compositional studies were carried out using field emission scanning electron microscopy (FESEM) and energy dispersive analysis of X-rays (EDAX), respectively. Lattice structure was confirmed via Raman characterization for the prepared samples. The sample formation was further verified through Fourier transform Infra-Red (FTIR) spectroscopy. The dielectric studies reveal the $\text{La}_{0.9}\text{Na}_{0.1}\text{CrO}_3$ (13×10^4) and $\text{Ni}_{0.5}\text{Cu}_{0.5}\text{Fe}_2\text{O}_4$ (1.83×10^4) exhibit high dielectric constant. However, their composites show abrupt drop in dielectric constant. The electric modulus study confirmed that the samples exhibit non-Debye character with spread of relaxation time constants.

Keywords: Structure; Rietveld refinement; morphology; dielectric properties.

1. Introduction

Metal oxides of ABO_3 type usually called perovskite compounds have in particular gained the attention of the scientific community and industrialists owing to their intriguing physical and chemical properties in the recent past. They exhibit features such as high temperature processability, optical, magnetic, electrical properties which are subject of doping of variety of impurities like alkali, alkaline and transition metals, lanthanides, etc.^{1,2} Doping various transition metals with different concentrations and possessing different crystal structures such as cubic, hexagonal, orthorhombic, rhombohedral and so on also impact their properties to a great extent. It is because of these prospective features, perovskite compounds with time are finding new application areas in modern technology and industry.^{3,4}

Perovskite rare earth chromites have been prepared and were deeply studied. The main concentration was focused on their preparation procedures, catalytic properties and their effects on the basic physical and chemical properties.^{5,6} In this chromite family, LaCrO_3 -based perovskite materials were the most important compounds by virtue of its intriguing electrical and chemical properties.^{6,7} Due to its ubiquitous properties, LaCrO_3 has found applications in many modern day applications such as solid-oxide catalysis, sensors, etc.^{7,8} Despite their huge applications, they are yet to be explored in terms of doping, concentration of dopants and preparation condition and their biphasic compounds.⁹

Spinel ferrites of type AB_2O_4 possess a structure of close packed cubic arrangement. Ferrites are commercially important, as they possess a substantial room temperature spontaneous magnetization. Soft magnetic ferrites have applications in magnetic resonance image (MRI), biomedicine, catalysis, medical diagnostics, drug delivery and other high magnetic moment applications.¹⁰ Spinel ferrites of the type AB_2O_4 exhibit versatile structural, electric and magnetic properties owing to its feasibility to make a huge number of solid solutions of different metal cations and a large compositional variability.

Nickel ferrites substituted with copper are an important class of spinel ferrites. Nickel ferrite is an inverse spinel ferrite and has a very high electrical resistivity and very low eddy current losses.¹¹ Ferrite (bulk) crystals in general and their nanocrystals in particular have many applications in bioseparation, inter-body drug delivery^{12,13} and magnetic refrigeration systems.¹⁴ Likewise, Nickel ferrites doped with copper proved to be better softer magnetic materials.¹⁵ Both the magnetic and structural properties of the spinel ferrites depend on the magnetic interaction and cation distribution in the tetrahedral (A) and octahedral (B) sites.

Multiferroic magnetoelectrics which display simultaneous magnetic and electric ordering are the most important materials from scientific and technological point of view. The co-existence of magnetic and electric phases facilitates the material with the “product” property. In other words,

the composite exhibits responses that are not available in the individual phases and hence their combination allows an additional degree of freedom in the design of actuators, transducers and storage devices. However, the choice of single-phase materials exhibiting coexistence of strong ferromagnetic, ferrimagnetic and ferroelectricity is limited.^{16,17}

From the perspective of important scientific and technological conclusions, ferroelectric (FE) and ferromagnetic (FM) materials have been the hot topic among the materials scientists. Usually, ferroelectricity results from relative shifts of negative and positive ions inducing surface charges requiring empty *d* orbitals. On the other hand, magnetism is subject of ordering of spins of electrons in incomplete ionic shells resulting from partially filled *d* orbitals. Another advanced family of multifunctional materials, usually called as magnetoelectric (ME) multiferroics possess simultaneously ferroelectric and ferromagnetic properties in the same phase and exhibit linear coupling between them. Such materials display the magnetoelectric (ME) coupling in which the spontaneous magnetization can be switched by an applied electric field and the spontaneous electrical polarization can be switched by an applied magnetic field, due to the cross coupling between FE and FM ordering and are expected to revolutionize the technology.^{18,19}

In this report, the monovalent alkali metal Na⁺-doped LaCrO₃ and transition metal Cu²⁺-doped NiFe₂O₄ are discussed. These materials are characterized by XRD, Raman spectroscopy, FTIR, FESEM, EDAX for structural studies and for electrical properties, these materials are subjected to the dielectric and electric modulus studies. The same studies were carried for their $(1-x)$ La_{0.9}Na_{0.1}CrO₃ + (x) Ni_{0.5}Cu_{0.5}Fe₂O₄ ($x = 0.25, 0.5$) composites. Their technological fragrance mentioned above was a motivation to study them individually and in the biphasic composites. The La_{0.9}Na_{0.1}CrO₃ and Ni_{0.5}Cu_{0.5}Fe₂O₄ and their composite as $(1-x)$ La_{0.9}Na_{0.1}CrO₃ + (x) Ni_{0.5}Cu_{0.5}Fe₂O₄ ($x = 0.25, 0.5$) have been synthesized by the conventional solid state reaction route.

2. Experimental Details

The polycrystalline samples of Ni_{0.5}Cu_{0.5}Fe₂O₄, La_{0.9}Na_{0.1}CrO₃ and their composites $(1-x)$ La_{0.9}Na_{0.1}CrO₃ + (x) Ni_{0.5}Cu_{0.5}Fe₂O₄ ($x = 0.25, 0.5$) were successfully prepared via solid state reaction route. The starting materials were highly pure ($\approx 99\%$) with the molecular formulas La₂O₃, CuO, Cr₂O₃, Fe₂O₃, NiO, Na₂CO₃. These materials were mixed according to the molecular formula of the compound after being weighed in the stoichiometric ratios.

The Ni_{0.5}Cu_{0.5}Fe₂O₄ was calcined at 1000°C for 10 h after grinding it for 5 h followed by regrinding for the same time and recalcination at 1100°C for 10 h. The powder was mixed with PVA as binder and pressed into circular discs of 10 mm diameter under the hydraulic press at 7 tons per inch. The so obtained pellets were sintered for 12 h at 1200°C and

then silver pasted for good electrical contact for the dielectric measurements. The same procedure was followed for the La_{0.9}Na_{0.1}CrO₃ with double calcination at a temperature of 900°C via intermediate grinding of 5 h each and sintering temperature of 1000°C for 12 h. The calculated amounts of both the phases according to the formula $(1-x)$ La_{0.9}Na_{0.1}CrO₃ + (x) Ni_{0.5}Cu_{0.5}Fe₂O₄ ($x = 0.25, 0.5$) were mixed for 5 h followed by calcination at 500°C. The fine powder of mixture was pelletized as mentioned above. The sintering temperature for composites was taken to be 800°C to maintain both the phases with uniform dispersion through grinding.

Crystal structures of the as prepared powders was analyzed by powder X-Ray diffraction characterization technique using Bruker D8 Advanced X-Ray diffractometer with Cu-K α 1 radiation of wavelength $\lambda = 1.5406 \text{ \AA}$ over angular range “ 2θ ” from 10–80°. Rietveld refinement was done using software FullProf. Energy dispersive analysis of X-ray spectra was obtained using energy dispersive spectrometer, model INCA Oxford. Raman spectroscopy of synthesized samples was carried out employing Jobin Yvon Horiba Lab RAM (system HR800) spectrometer with a 488 nm excitation source. Dielectric measurements were carried out by Wayne Kerr Model 6500 B, precision impedance analyzer with the frequency range 20 Hz–1 MHz. Fourier transform infrared spectroscopy was carried by Perkin Elmer FT-IR/FIR spectrometer (frontier) in the range of 400–4000 cm^{−1}.

3. Results and Discussions

3.1. X-Ray diffraction

The polycrystalline single phased parent compounds namely, Ni_{0.5}Cu_{0.5}Fe₂O₄, La_{0.9}Na_{0.1}CrO₃ and their biphasic composites viz. $(1-x)$ La_{0.9}Na_{0.1}CrO₃ + (x) Ni_{0.5}Cu_{0.5}Fe₂O₄ ($x = 0.25, 0.5$) were X-ray diffraction characterized. To confirm phase formation and type of crystal structure, the XRD spectra was analyzed and the analysis revealed the structure of parent Ni_{0.5}Cu_{0.5}Fe₂O₄ to be cubic with the assigned space group of *Fd-3m* while the La_{0.9}Na_{0.1}CrO₃ chromite has crystallized in an orthorhombically distorted perovskite structure with space group *Pnma*. However, the dual phase of the composites have been retained. The reflections peaks in the Ni_{0.5}Cu_{0.5}Fe₂O₄ and La_{0.9}Na_{0.1}CrO₃ samples and the assigned space groups are well matched with JCPDS card 24-1016. The lattice parameters calculated are in agreement with the reports.^{20,21} The XRD characteristic peaks for both parents and their composites have been found to be intense which reveals highly crystalline nature of the samples while the narrowness of the FWHM of these main peaks suggests the larger values of the average crystallites. The average particle size has been calculated using classical Scherrer's formula $t = 0.9\lambda/\beta \cos \theta$, where t is the average crystallite size, $k = 0.9$ is a constant (shape factor), λ is the wavelength of X-Rays used (1.5406 Å), θ is the angle of

diffraction, β is the FWHM and the average particle size calculated are 44.41, 139.52, 44.052 and 43.123 nm for $\text{La}_{0.9}\text{Na}_{0.1}\text{CrO}_3$, $\text{Ni}_{0.5}\text{Cu}_{0.5}\text{Fe}_2\text{O}_4$ and their $(1-x)$ $\text{La}_{0.9}\text{Na}_{0.1}\text{CrO}_3 + (x)$ $\text{Ni}_{0.5}\text{Cu}_{0.5}\text{Fe}_2\text{O}_4$ ($x = 0.25, 0.50$) samples, respectively.^{20,22} From the XRD pattern, it is clear that the crystallinity has been reduced in composites compared to the comprising parent compounds inferred from diminished peak intensities. This means that the composites are porous in nature and are expected to exhibit the increased conductivity that will greatly influence the dielectric nature of the parent compounds.

The XRD data was Retveld refined using FullProf software²³ and the plots are displayed in Fig. 1. The various parameters obtained confirmed the type of phase, crystal structure and the dual phase of the composites. The details of

the parameters obtained from the Retveld refinement are scripted in Table 1. The crystal structure of the parent compounds was developed using the VESTA software and has been displayed as top view and 3D structure in Fig. 2.

3.2. Microstructure, morphology and composition

Energy dispersive analysis of X-rays (EDAX) is a technique that confirms the composition of the sample and later helps us to determine the influence of the dopants in minute quantities. In this context, we characterized our $\text{Ni}_{0.5}\text{Cu}_{0.5}\text{Fe}_2\text{O}_4$, $\text{La}_{0.9}\text{Na}_{0.1}\text{CrO}_3$ and their $(1-x)$ $\text{La}_{0.9}\text{Na}_{0.1}\text{CrO}_3 + (x)$ $\text{Ni}_{0.5}\text{Cu}_{0.5}\text{Fe}_2\text{O}_4$ ($x = 0.25, 0.50$) samples for compositional verification using EDAX technique. Figure 3 represents the EDAX spectra of the parent samples and their composites

Fig. 1. Retveld refinement of the X-ray data displayed.

Table 1. Details of Rietveld refinements of $\text{Ni}_{0.5}\text{Cu}_{0.5}\text{Fe}_2\text{O}_4$, $\text{La}_{0.9}\text{Na}_{0.1}\text{CrO}_3$ and their composites $(1-x)\text{La}_{0.9}\text{Na}_{0.1}\text{CrO}_3 + (x)\text{Ni}_{0.5}\text{Cu}_{0.5}\text{Fe}_2\text{O}_4$ ($x = 0.25, 0.50$).

Parameters	Values obtained at different temperatures					
	LNCO	NCFO	0.75LNCO+0.25NCFO		0.5LNCO+0.5NCFO	
			Phase 1	Phase 2	Phase 1	Phase 2
Space group	<i>Pnma</i>	<i>Fd3m</i>	<i>Pnma</i>	<i>Fd3m</i>	<i>Pnma</i>	<i>Fd3m</i>
<i>a</i> (Å)	5.499(3)	8.53(2)	5.514(3)	8.34(2)	5.515(3)	8.338(3)
<i>b</i> (Å)	5.487(3)	8.53(2)	5.475(3)	8.34(2)	5.476(3)	8.338(3)
<i>c</i> (Å)	7.759(3)	8.53(2)	7.75(2)	8.34(2)	7.753(3)	8.338(3)
<i>V</i> (Å ³)	234.14	582.31	233.996	580.773	234.116	579.74
Density (g/cm ³)	3.718	4.59	3.788	3.82	4.199	3.88
<i>R_F</i>	11.4	10.3	10.9	11.7	10.7	9.54
<i>R_{Bragg}</i>	13.3	11.9	9.59	13.7	10.3	9.57
<i>R_{wp}</i>	11.5	39.0	36.4	43.7	24.3	28.5
<i>R_{exp}</i>	5.64	23.5	34.74	36.6	21.7	32.8
<i>R_p</i>	23.5	50.5	44.8	49.4	23.0	45.5
χ^2	4.09	3.9	1.5	1.43	1.26	1.38
GOF	2.2	2.1	1.2	1.2	1.2	1.2

under investigation. A thorough look clarifies that all the components of the parent compounds and their composites have been retained and within the experimental limits, there is no loss of any of the integral elements. The presence of elements and their composition is depicted by the intensity of the peaks in the spectra. Thus, this very characterization opens the window to test the samples under observation for the other physical properties and the influence of phases and dopants.

We further characterized our materials for microstructural and morphological studies using the sensitive and effective field emission scanning electron microscopy (FESEM). The images of the samples obtained are depicted as the insets of the corresponding EDAX spectrum in Fig. 3. A close observation of the micrographs revealed the effect of the sintering at higher temperature in the parent compounds in the sense of the growth in the average particle size. The micrographs further revealed that there is no visible grain boundary and the crystals are well separated from one another. Further the growth in average particle size is obviously larger in LNCO when compared to NCFO. From the micrographs of the composites, one can say that dispersion of NCFO phase in the LNCO phase is almost uniform and again the grown particles are separated which may be attributed to the lower temperature treatment of the composites at 800°C. In the nutshell, all the FESEM images reveal the dominance of the agglomeration phenomena. We further investigated our samples for the average particle size using ImageJ software and found the particle size of $\text{Ni}_{0.5}\text{Cu}_{0.5}\text{Fe}_2\text{O}_4$, $\text{La}_{0.9}\text{Na}_{0.1}\text{CrO}_3$ and their $(1-x)\text{La}_{0.9}\text{Na}_{0.1}\text{CrO}_3 + (x)\text{Ni}_{0.5}\text{Cu}_{0.5}\text{Fe}_2\text{O}_4$ ($x = 0.25, 0.50$) to be 3.1, 2.69, 2.32 and 2.44 μm , respectively.^{24,25}

3.3. Fourier transform infra-red spectroscopy

To investigate the chemical environment of $\text{Ni}_{0.5}\text{Cu}_{0.5}\text{Fe}_2\text{O}_4$, $\text{La}_{0.9}\text{Na}_{0.1}\text{CrO}_3$ and their composites viz. $(1-x)\text{La}_{0.9}\text{Na}_{0.1}\text{CrO}_3 + (x)\text{Ni}_{0.5}\text{Cu}_{0.5}\text{Fe}_2\text{O}_4$ ($x = 0.25, 0.50$), the Fourier Transform Infra-Red (FTIR) spectra for the solid state reaction route products calcined at 1100°C are recorded in the range of 400–4000 cm^{-1} and displayed in Figs. 4(a) and 4(b), where Fig. 4(a) represents pristine compounds and Fig. 4(b) represent composites. For NCFO, intrinsic stretching vibrations of the metal at the tetrahedral site, $\text{M}_{\text{tetra}}\leftrightarrow\text{O}$, ν_1 , are generally observed in the range of 620–550 cm^{-1} .^{26,27} Octahedral-metal stretching vibrations, $\text{M}_{\text{octa}}\leftrightarrow\text{O}$, ν_2 -lowest band, are generally observed in the range of 450–385 cm^{-1} . In Fig. 4, ν_1 stretching vibration of ferrite was observed at 560 cm^{-1} and ν_2 stretching vibration was observed around 400 cm^{-1} for the spinel structure.^{28,29}

The FTIR spectrum of LaNaCrO_3 in Fig. 4 reveals several main absorption peaks between 400 and 4000 cm^{-1} , with the absorption bands at 405 and 564 cm^{-1} assigned to the O–Cr–O and Cr–O stretching modes of vibration, respectively. The higher frequency band lies in the range of 800–475 cm^{-1} with a center of 540 cm^{-1} due to a stretching vibration, whereas the low frequency band extends from 475 cm^{-1} to 300 cm^{-1} with a center of 400 cm^{-1} due to a bending vibration of metal oxygen bonds.^{30,31} The absorption bands fulfil the criteria of desired bond formation and hence confirms the structure/formation of the perovskite material LNCO.

However in the composites the absorption bands have merged as they were in the vicinity of the one another. As the bands of the two phases of the composite is indistinguishable, we assign them the stretching and vibrations as discussed above for the both samples separately.

Fig. 2. Crystal structure of orthorhombic $\text{La}_{0.9}\text{Na}_{0.1}\text{CrO}_3$ and cubic $\text{Ni}_{0.5}\text{Cu}_{0.5}\text{Fe}_2\text{O}_4$.

4. Raman Scattering Spectra

The ideal cubic structure of ABO_3 perovskites is simple with corner-linked anion octahedra BO_6 , the B cations at the center of the octahedra and the A cations in the space between the octahedra. In this structure, Raman scattering is forbidden by symmetry. RCrO_3 chromites crystallize in an orthorhombically distorted perovskite structure with space group $Pnma$.

In comparison to the ideal cubic $Pm\bar{3}m$ perovskite structure, the orthorhombic $Pnma$ structure is obtained by an anti-phase tilt of the adjacent CrO_6 octahedra.³² The tilting of the CrO_6 octahedra necessarily induces a distortion of the RO_{12} polyhedra. In the $Pnma$ structure, the A-site element is considered to be in eight-coordination. A Jahn-Teller (JT) inactive Cr^{3+} prohibits dispersion in the Cr–O bonds nearly by an order of

Fig. 3. FESEM and EDAX of $\text{Ni}_{0.5}\text{Cu}_{0.5}\text{Fe}_2\text{O}_4$, $\text{La}_{0.9}\text{Na}_{0.1}\text{CrO}_3$ and their composites $(1-x)\text{La}_{0.9}\text{Na}_{0.1}\text{CrO}_3 + (x)\text{Ni}_{0.5}\text{Cu}_{0.5}\text{Fe}_2\text{O}_4$ ($x = 0.25, 0.50$).

Fig. 4. FTIR spectroscopy of (a) $\text{Ni}_{0.5}\text{Cu}_{0.5}\text{Fe}_2\text{O}_4$, $\text{La}_{0.9}\text{Na}_{0.1}\text{CrO}_3$ and (b) $(1-x)\text{La}_{0.9}\text{Na}_{0.1}\text{CrO}_3 + (x)\text{Ni}_{0.5}\text{Cu}_{0.5}\text{Fe}_2\text{O}_4$ ($x = 0.25, 0.50$) synthesized samples displayed in Fig. 1.

Fig. 5. Raman scattering of the samples of $\text{Ni}_{0.5}\text{Cu}_{0.5}\text{Fe}_2\text{O}_4$, $\text{La}_{0.9}\text{Na}_{0.1}\text{CrO}_3$ and their composites $(1-x)\text{La}_{0.9}\text{Na}_{0.1}\text{CrO}_3 + (x)\text{Ni}_{0.5}\text{Cu}_{0.5}\text{Fe}_2\text{O}_4$ ($x = 0.25, 0.50$).

magnitude lower compared to observations in JT-active orthomanganites. All three distortions (tilt, octahedra distortion and A-cation displacement) break the cubic symmetry and thus activate zone center Raman modes. According to group theory, the orthorhombic $Pnma$ structure with four formula units per unit cell give rise to 24 Raman-active modes $7 A_g + 5 B_{1g} + 7 B_{2g} + 5 B_{3g}$.³³

Figure 5 shows Raman spectra for $\text{Ni}_{0.5}\text{Cu}_{0.5}\text{Fe}_2\text{O}_4$ and $\text{La}_{0.9}\text{Na}_{0.1}\text{CrO}_3$ samples prepared by solid state synthesis route. For orthorhombic structural $\text{La}_{0.9}\text{Na}_{0.1}\text{CrO}_3$, we observed rotational vibration at 585 cm^{-1} represented as B_{3g} (3) assigned to O_2 and O_1 anti-stretching, mode at 433 cm^{-1} depicted as A_g (6) is attributed to BO_6 bendings, a mode at 242 cm^{-1} is due to atomic motions along axes, i.e., $\text{O1}(x)$, $\text{A}(-x)$ activated by distortion and assigned to A shift presented as A_g (4), the mode of vibration at 160 cm^{-1} [A_g (2)] exists due to $\text{A}(z)$ out of plane motion that the bands observed above 600 cm^{-1} are unlikely to be due to the normal modes of vibration for $\text{La}_{0.9}\text{Na}_{0.1}\text{CrO}_3$.^{32,33} Bands in the range $600\text{--}200\text{ cm}^{-1}$ have been reported for the Raman spectra of lanthanum–chromium oxide compounds. Therefore, bands observed in the spectrum of $\text{La}_{0.9}\text{Na}_{0.1}\text{CrO}_3$ could be due to the presence of higher oxidation state of chromium.^{34,35}

A spinel $\text{Ni}_{0.5}\text{Cu}_{0.5}\text{Fe}_2\text{O}_4$ compound crystallized into cubic structure with a space group of O^7h ($Fd\text{-}3m$) and group theory predicts five active Raman modes viz. $A_{1g} + E_g + 3T_{2g}$.³⁶ To simplify, peaks are assigned as for normal spinel structure. But, all five Raman peaks are asymmetric. Microscopically, the structure of $\text{Ni}_{0.5}\text{Cu}_{0.5}\text{Fe}_2\text{O}_4$ can be considered as a mixture of two sublattices with Fe^{3+} and $\text{Ni}^{2+}/\text{Cu}^{2+}$. It is supposed that Fe^{3+} and $\text{Ni}^{2+}/\text{Cu}^{2+}$ are ordered over the A- and B-sites. The A_{1g} [698 cm^{-1}] mode is due to symmetric stretching of oxygen atoms along Fe–O (and Ni/Cu–O) bonds

in the tetrahedral coordination. E_g [331 cm^{-1}] is due to symmetric bending of oxygen with respect to the metal ion and F_{2g} (3) [566 cm^{-1}] is caused by asymmetric bending of oxygen. F_{2g} (2) [480 cm^{-1}] is due to asymmetric stretching of Fe (Ni/Cu) and O. F_{2g} (2) and F_{2g} (3) correspond to the vibrations of octahedral group. F_{2g} (1) [203 cm^{-1}] is due to translational movement of the tetrahedron (metal ion at tetrahedral site together with four oxygen atoms). All five Raman peaks are asymmetric, with shoulder on the low energy side. At a microscopic level the structure of $\text{Ni}_{0.5}\text{Cu}_{0.5}\text{Fe}_2\text{O}_4$ can be considered as a mixture of two sublattices with Fe^{3+} and Ni^{2+} . It is supposed that Fe^{3+} and Ni^{2+} are ordered over the B-sites. In nanocrystalline samples asymmetry is partly due to confinement and size-distribution of nanoparticles.^{37,38}

The Raman inelastic scattering spectra of composites display the individual modes for the comprising phases as well as mixed behavior. The parent compounds display sharp modes of vibration which are suppressed in the case of composites depicting their porous character.

5. Dielectric Properties

The most important property of ferrites is the dielectric behavior which relies on the preparation procedure and environment, crystallite size, composition and temperature treatment. The dielectric constant (ϵ') is determined by using the formula $\epsilon' = Cd/\epsilon_o A$, where C is the capacitance of the pellets, d is the thickness of the pellets, A is the cross-sectional area of the circular surface of the pellets and ϵ_o is the permittivity of free space.

Figures 6(a) and 6(b) represent frequency dependence of the dielectric constant (ϵ') in the frequency range from 20 Hz to 1 MHz for parent and composite materials. The general overview of the plots reveal that the dielectric constant at low frequencies is higher and decreases sharply with increase in frequency and attains a constant character at higher frequencies for parent as well as composite materials. The decrease in dielectric constant is rapid at lower frequencies showing dispersion in the lower frequency region. At higher frequencies, the decrease in dielectric constant with increase in frequency occurs as the electrons beyond a certain critical frequency do not obey the alteration of applied *ac* electric field. This decreases the possibility of electrons reaching the grain boundary and hence polarization decreases.^{39,40} This dependence of dielectric constant on the applied field can be attributed to the interfacial polarization as per the Maxwell–Wagner and Koop’s phenomenological theory.^{22,40}

In the as-prepared materials, we observed higher dielectric constant for $\text{La}_{0.9}\text{Na}_{0.1}\text{CrO}_3$ (13×10^4 at 20 Hz) and that for $\text{Ni}_{0.5}\text{Cu}_{0.5}\text{Fe}_2\text{O}_4$ (1.83×10^4 at 20 Hz). However, their composites extremely low dielectric constant values compared to their parent materials. This abrupt decrease in the dielectric constant can be attributed to the lower bandgap of

Fig. 6. Dielectric constant of (a) $\text{Ni}_{0.5}\text{Cu}_{0.5}\text{Fe}_2\text{O}_4$, $\text{La}_{0.9}\text{Na}_{0.1}\text{CrO}_3$ and (b) $(1-x)\text{La}_{0.9}\text{Na}_{0.1}\text{CrO}_3 + (x)\text{Ni}_{0.5}\text{Cu}_{0.5}\text{Fe}_2\text{O}_4$ ($x = 0.25, 0.50$) composites.

the NCFO compared to the higher bandgap of the matrix $\text{La}_{0.9}\text{Na}_{0.1}\text{CrO}_3$. In the composite system, the inter-diffusion of phases reduce bandgap value and in the response of which the movement of electrons becomes easier.^{41,42} The lower value of ε' of $(0.75)\text{La}_{0.9}\text{Na}_{0.1}\text{CrO}_3 + (0.25)\text{Ni}_{0.5}\text{Cu}_{0.5}\text{Fe}_2\text{O}_4$ compared to $(0.5)\text{La}_{0.9}\text{Na}_{0.1}\text{CrO}_3 + (0.5)\text{Ni}_{0.5}\text{Cu}_{0.5}\text{Fe}_2\text{O}_4$ can be due to lesser crystallinity and nonuniform distribution of NCFO phase in the LNCO matrix as revealed from the FESEM micrographs. The mechanism through which the polarization takes place is similar to that in conduction process which highly relies on the synthesis method, chemical composition, crystallite size and cation distribution.^{43,44} It is the electronic exchange between metal ions in response of which the local displacement of the electrons in the direction of the applied field takes place and these electrons are responsible for electrical polarization. The other reasons of the high value of dielectric constant at low frequency may be due to the predominance of cations, oxygen vacancies, dislocations, voids and grain boundary defects presents in the crystal structure.^{44,45}

The dielectric loss ($\tan \delta$) can be calculated by using the equation, $\varepsilon'' = \varepsilon' \tan \delta$, where $\varepsilon'' = (\omega R_p C_o)^{-1}$ and $C_o = \varepsilon_o A/d$. The frequency dependent variation of dielectric loss ($\tan \delta$) with frequency ($\log f$ (Hz)) has been displayed in Fig. 7. The frequency dependence of dielectric loss of $\text{Ni}_{0.5}\text{Cu}_{0.5}\text{Fe}_2\text{O}_4$, $\text{La}_{0.9}\text{Na}_{0.1}\text{CrO}_3$ and their $(1-x)\text{La}_{0.9}\text{Na}_{0.1}\text{CrO}_3 + (x)\text{Ni}_{0.5}\text{Cu}_{0.5}\text{Fe}_2\text{O}_4$ ($x = 0.25, 0.50$) samples at various temperatures is rather high at low frequency but falls quickly with rising frequency similar to the dependence of dielectric constant on frequency and attains a constant value at higher frequency regions. The $\tan \delta$ values tend to decrease with increasing frequency due to the space charge polarization. The trend that higher the ε' , higher is the loss is followed by the as prepared samples. It is seen that $0.5\text{LNCO} + 0.5\text{NCFO}$ composite exhibits a shoulder like

behavior which indicates the relaxation in the sample. In this sample, the loss value increases with frequency and attains a maximum value corresponding to a certain frequency and hereafter decreases with further increase in the frequency. This hump character in the loss value is attributed to the resonance between the frequency of the applied electric field and the hopping frequency localized charge carriers.^{46–48} Generally, the low loss is observed at higher frequencies which can be the response to the inhibition of the motion of domain wall. The decrease in dielectric loss tangent in response to the frequency can be well explained by Koop's law. Dielectric loss occurs as polarization lags behind the applied alternating field as well as due to the presence of impurities and structural inhomogeneties.^{44,45,49}

Fig. 7. Dielectric loss ($\tan \delta$) of $\text{Ni}_{0.5}\text{Cu}_{0.5}\text{Fe}_2\text{O}_4$, $\text{La}_{0.9}\text{Na}_{0.1}\text{CrO}_3$ and their composites $(1-x)\text{La}_{0.9}\text{Na}_{0.1}\text{CrO}_3 + (x)\text{Ni}_{0.5}\text{Cu}_{0.5}\text{Fe}_2\text{O}_4$ ($x = 0.25, 0.50$) as a function $\log f$ (Hz).

Fig. 8. σ_{ac} conductivity of the samples of (a) $\text{Ni}_{0.5}\text{Cu}_{0.5}\text{Fe}_2\text{O}_4$, $\text{La}_{0.9}\text{Na}_{0.1}\text{CrO}_3$ and (b) $(1-x)\text{La}_{0.9}\text{Na}_{0.1}\text{CrO}_3 + (x)\text{Ni}_{0.5}\text{Cu}_{0.5}\text{Fe}_2\text{O}_4$ ($x = 0.25, 0.50$) composites.

The σ_{ac} conductivity of the as prepared samples was calculated using formula, $\sigma_{ac} = \epsilon' \epsilon_0 \omega \tan \delta$, and has been represented in Figs. 8(a) and 8(b) for pristine compounds and composites, respectively as a function of $\log f$ (Hz). As the frequency increases, the σ_{ac} conductivity was found to be constant up to certain frequency value for all the prepared samples and then increases with further increase in frequency. This behavior could be due to activation of hopping of charge carriers between different localized states and after threshold frequency, the trapped charge carriers starts being free as a result of which the conductivity rises with further increase in frequency. Furthermore, the σ_{ac} conductivity tends to attain maximum value with increasing frequency as the immigration of electrons is increased.^{39–45,49}

The σ_{ac} conductivity can be seen increasing with increase in frequency and becomes independent of frequency after a certain value. The lower part of frequency will give direct current conductivity (σ_{dc}). The σ_{ac} conductivity can be well explained in terms of the relation so-called “universal dielectric response (UDR)” law $\sigma_{ac}(f) = \sigma_{dc} + \sigma_0 f^s$, where σ_0 is pre-exponential factor, s is an exponent that depends on both frequency and temperature in the range $0 < s \leq 1$, σ_{dc} is the dc bulk conductivity and f is the frequency. The UDR governs thermally assisted tunneling between localized states and thereby describes phenomenon associated with interactions between charges and dipoles.^{50–57} The σ_{ac} conductivity of the composites is observed to be decrease compared to the parent compounds. The overall electrical properties of the materials under study are somewhat interesting in terms of part electric dielectric constant and loss tangent value.

6. Electrical Modulus Studies

Electrical response of the materials can also be analyzed through electric modulus, which provides another approach based on polarization analysis. Complex electric formalism

gives information about homogeneous or inhomogeneous nature of the polycrystalline ceramics, which can be probed into bulk and grain boundary effects. This formalism also provides wider insights on charge transport processes such as mechanism of conductivity and relaxation as a function of frequency. In the modulus formalism, an electric modulus M^* is defined as the inverse of the complex dielectric permittivity ϵ^* formulated by Macedo *et al.*⁵⁸

$$M^* = (\epsilon^*)^{-1} = (\epsilon' - i\epsilon'')^{-1} = M' + iM'',$$

where M' and M'' are the real and imaginary part of complex modulus and are used to formulate Cole–Cole plots.

Figures 9(a) and 9(b) show the variation of the real part of the electric modulus as a function of frequency. The plots reveal that M' shows a dispersion behavior tending towards M_∞ , (M_∞ = the asymptotic value of M' at higher frequencies). At low frequencies, the electrode effects are dominant and M' approaches to zero. It can be seen that the interfacial effects tend to be eliminated in modulus representation.^{59,60} The lower value of M' at low frequency shows no contribution from electrode polarization. The conductivity relaxation phenomenon is obvious from the continuous dispersion on increasing frequency which is attributed to be the scarcity of restoring force governing the mobility of charge carriers under the influence of induced electric field.^{60–62} This behavior is attributed to conduction as a result of short-range mobility of charge carriers. The lower frequency region is the regime where conduction mechanism is governed by long-range hopping of charge carrier mobility.

Variation of imaginary part of electric modulus M'' as a function of frequency for $(0.75)\text{LNCO} + (0.25)\text{NCFO}$ and $(0.5)\text{LNCO} + (0.5)\text{NCFO}$ is shown in Fig. 9(d). At a particular frequency, the single peak in M'' versus frequency plot can be seen. The appearance of the peak suggests the conductivity relaxation phenomenon in the material. This graph shows that the modulus peaks lower in intensity but shifts

Fig. 9. Electric modulus M' versus $\log f$ (Hz) for (a) LNCO and NCFO, (b) $(1-x)$ LNCO + (x) NCFO ($x = 0.25, 0.50$), and M'' versus $\log f$ (Hz) viz. (c) LNCO, NCFO and (d) $(1-x)$ LNCO + (x) NCFO ($x = 0.25, 0.50$) samples.

towards higher frequency side on increasing concentration of NCFO.^{58,61} The asymmetric broadening of the peak indicates the spread of relaxation with different time constants and relaxation in the material is of non-Debye type. In low frequency region the charge carriers are mobile over long distances and are associated with hopping conduction process.^{59–62} Almost same behavior is displayed by LNCO and NCFO as depicted in Fig. 9(c) but the peaks are highly diminished. For high frequency region, the carriers are confined to potential wells and are mobile over short distances associated with relaxation polarization process which is in good agreement with dielectric properties. The portion of broad peak indicates the transition of the mobility of the charge carriers from long range to short corresponds to applied field. The witnessed broadness of the peak is indicative of the spread of the relaxation.^{61,62}

Figure 10(a) shows the complex modulus plots (M' versus M'') for LNCO and NCFO. Two well resolved semicircles are

observed among which the first semicircle lies in the low frequency region which indicates the capacitive grain boundary effect and the second one represents the capacitive grain effect at higher frequency side. Thus, we observed grain boundary and grain effects at lower and higher frequencies, respectively. The smaller semicircle from grain boundary effect at lower frequencies shows increasing trend. The double semicircles in Fig. 10(a) shows the dominant grain contribution since modulus plot focus the smallest capacitance. Complex modulus analysis is suitable when materials have nearly similar resistance but different capacitance.⁶²

Figure 10(b) shows the Cole–Cole plot of complex modulus for (0.75) LNCO + (0.25) NCFO and (0.5) LNCO + (0.5) NCFO composites. The curves do not form exact semicircles but possess a shape of deformed semicircle with their centers lying below x -axis. This shows a non-Debye type of relaxation in the materials having spread of relaxation with different time constants. The broadness of the curve

Fig. 10. Cole–Cole plots for (a) LNCO and NCFO and (b) $(1 - x)$ LNCO + (x) NCFO ($x = 0.25, 0.50$) samples.

peaks for both the materials and associated asymmetries and separations of peak maxima, support the departure from ideal Debye-like behavior. This nonideal behavior could be attributed to several factors such as grain orientation, grain boundary, stress–strain phenomena, and atomic defect distribution.^{62–64}

7. Conclusions

Successful synthesis of $\text{Ni}_{0.5}\text{Cu}_{0.5}\text{Fe}_2\text{O}_4$, $\text{La}_{0.9}\text{Na}_{0.1}\text{CrO}_3$ and their $(1 - x)$ $\text{La}_{0.9}\text{Na}_{0.1}\text{CrO}_3 + (x)$ $\text{Ni}_{0.5}\text{Cu}_{0.5}\text{Fe}_2\text{O}_4$ ($x = 0.25, 0.50$) materials by solid state reaction route is effectively carried out. The $\text{La}_{0.9}\text{Na}_{0.1}\text{CrO}_3$ compound crystallized into the orthorhombic structure with space group $Pnma$ while the $\text{Ni}_{0.5}\text{Cu}_{0.5}\text{Fe}_2\text{O}_4$ has been found to crystallize into the cubic structure ($Fd3m$) reconfirmed via Retveld refinement. The dual phase in the composites has been retained confirmed from XRD, Retveld refinement, as well as Raman scattering characterization techniques. FESEM confirmed the porosity of the composite samples and domination of agglomeration while as EDAX infers retainment of the integral elements of the materials under investigation. The dielectric characterization revealed the higher dielectric constant for LNCO and NCFO. However, their composites show sudden decrease in the said behavior attributed to the embedding of lower bandgap NCFO into the higher bandgap LNCO as well as the inter-diffusion of phases.

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