La$^{3+}$ effectiveness replacement on the ferrite material
\((Cu_{0.2}Zn_{0.45}La_xFe_{2-x}O_4)\) On the structural and electrical and magnetic features

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Abstract. Nano ferrite with chemical formula \((Ni_{0.35}Cu_{0.3}Zn_{0.45}La_xFe_{2-x}O_4)\), were chemically collected utilizing sol-gel auto–combustion procedure for the values of \((X=0.0, 0.025, 0.05\) and \(0.075)\). The prepared samples were calcined at \((900^\circ C)\) for \((2h)\), the formation of ferrite was assured using (XRD) and (SEM) techniques. X-ray diffractometer result shows that ferrite have spinal cubic phase with a particle size ranging from \((22-29\) nm), the Lattice constant and density \((\rho_x)\) increased with La$^{3+}$ content while the porosity was noticed to decrease. And have been studied dielectric properties. It was also observed that the value of the dielectric constant and the dielectric loss factor decreased by increasing the frequency. The increase in alternating conductivity \((\sigma_a.c)\) was also observed with increasing frequency.

1. Introduction
Rare-earth-materials have good dielectric characteristics with high electrical resistivity. Thus, these rare earth ions replacement into spinel ferrites may modify the magnetic and electrical features and also have big influential on the magnetic disparity system creating the spinel ferrite as favorable materials that can be replaced into the Hexa-ferrite or garnets [1,2]. Ferrites electrical properties depend on the micro-structure, chemical combination and assembly technique [3]. Lanthanum is considered the second lightest rare earth element in the lanthanide chain. It is silvery white color metal and can be found in monazite and bastnasite ores. This element has special quality comparing with other (REE), like being simple electronic spectrum which is beneficial for experiential analysis since it has the lowest vapor pressure and highest boiling point at its fusion point; and at atmospherically pressure lanthanum is considered the only superconducting among other (REE) [4].

Different procedures were used so as to synthesize the soft spinel ferrite materials (e.g. chemical co-precipitation [5], hydrothermal [6], mechano-chemical [7], micro emulsion [5], rheological phase reaction [8], and also sol-gel [9]).

2. Experimental

2.1 Materials and Synthesis:
The Nano-ferrites of the composition \((Ni_{0.35}Cu_{0.3}Zn_{0.45}La_xFe_{2-x}O_4)\) were \((X=0.0, 0.025, 0.05\) & \(0.075)\) that prepared using sol-gel-auto-combustion technique by below mentioned raw materials. In order to prepare \((Ni0.35 Cu0.2Zn0.45)La_x Fe_{2-x}O_4\) ferrite with \(x = 0.0, 0.025, 0.05\) and \(0.075\) compositions, it was used analytical stage for: \([Ni(NO3)2\cdot6H2O]\), \([Zn(NO3)2\cdot6H2O]\),
[Cu(NO₃)₂·3H₂O], [Fe(NO₃)₃·9H₂O], [C₆H₈O₇·H₂O] and [La(NO₃)₃]. It was solved citric acid and metal nitrates in deionized water, all these are collected in glass beaker and mixed well at room temperatures by hot plate magnetic stirrers with high speed. Ammonia solution was added slowly the form of drops into the mixed solution to control its pH until reach threatens from 7 with continuous rotation. Gradually increase in temperature to reaches of 80°C in order to turn it into a gel then was burnt in a self-propagating ignition way to get a formation of a feathery movable powder the as-burnt predecessor powder was later calcined at (900 °C) for 4 hours after that it was pressed using a die with (1.5cm) diameter to make specimens in a pellet shapes. The pressing load used was (7ton/cm²) and the specimens held for 2min. under pressure using a hydraulic press of a maximum load (15) ton.

2.2 Characterization:
The structural characterization of the prepared nano ferrites was performed by X-ray diffraction analysis and Scanning Electron microscopic analysis and EDX technique. XRD analysis confirms the phase formation and SEM analysis reveals the structural morphology. Nano-ferrites dielectric features were deliberated by LCR meter range of 50 KHz to 1MHz. Dielectric parameters like constant (ε′) and loss tangent (tan δ) were calculated using LCR meter

3. Results and discussion:

3.1 Structural analysis
XRD prototypes of \( \text{Ni}_{0.35} \text{Cu}_{0.20} \text{Zn}_{0.45} \text{La}_{x} \text{Fe}_{2-x} \text{O}_4 \) Nano crystals, for all the samples with \( x = 0.00, 0.025, 0.050, \) & \( 0.075 \) as in Figure 1. (XRD) patterns disclose a single stage cubic spinel arrangement with few traces of minor stage. In addition, diffraction peaks that were noticed could be allocated to the reflection flat surface of \([111, 220, 311, 400, 422, 511\) and 440\] which might be indexed to a single-stage Ni-Cu-Zn ferrite nano-crystal. in the interim, the peak matching to \( 2θ = 32.21 \) is due to minor stage at the grain limitations for \( \text{(+) LaFeO}_3 \) (ICDD PDF #37±1493) excluding for the cubic spinel phase. \( \text{LaFeO}_3 \) intensity peak has risen with the increasing in \( \text{La}^+3 \) ion concentration [10].

![Figure 1. (XRD) patterns sample of Ni₃₀Cu₀₂₀Zn₄₅LaₓFe₂₋ₓO₄](image)

The individual lattice parameter structure was detected as the relation below: [11].

\[
d_{hkI} = \frac{\alpha}{\left( h^2 + k^2 + l^2 \right)^{1/2}}
\]

\(\alpha = \text{lattice constant}, \ (d) = \text{inter-planar distance and} \ (h, \ k, \ l) \text{are the Miller indicators} \)
The sample's rate crystallite size is determined using the Scherer's equation [12].

\[ D = \frac{\alpha}{\beta \cos \theta} \]  

Where \(D\) = crystallite size, \(\beta\) = diffraction line full width at maximum half intensity that is counted in radians, is x-ray wavelength (Cu kα radiation, 1.5405Å) and \(\theta\) is the Bragg angle, and Williamson-Hall formula

\[ \beta_n \cos \theta = \frac{K\lambda}{D} + [4\pi sin \theta] \]  

The actual (X-ray) density of the samples was calculated using the formula [13],

\[ \rho_{x-ray} = \frac{ZM_{nit}}{N_{Av}V} \]  

Here; \(M\) = sample molecular weight per (Kg), \(N\) = number of Avogadro (per mol) and \(a\) = lattice parameter (Å). The samples bulk densities as the following formulation,

\[ \rho_b = \frac{m}{\pi r^2 h} \]  

\(m\) = mass per (Kg), \(r\) = radius (m) and \(h\) = the pellet height per (m).

The following relation can calculate the porosity percentage [14]

\[ P = 1 - \frac{\rho_b}{\rho_{x-ray}} \times 100\% \]  

The observed increase in the lattice constant (a) that might be related with the La+3 increasing contentment where the La+3 ionic radius (1.6061) can be bigger in comparing with the one of Fe+3ion (0.645) that replacing iron ions on octahedral B-site which in turn can cause inequality in the structure. For this reason, the lattice constant has to be enlarged with the La+3 increasing contentment through the exchange operation [15, 16]. The samples crystallite size can be observed with lanthanum concentration increasing. This is consistent with the results reported for La+3 doped Ni–Cu–Zn ferrite [17]. The X-ray density increases linearly with lanthanum ion content and this can be correlated with the increase of atomic weight of La+3 substituted for Fe+3 of lower atomic mass. The magnitudes of bulk densities are smaller than that of the corresponding X-ray densities and this difference in magnitude may be attributed to the existence of pores in the bulk samples. The porosity is observed to decrease with La+3 content.

**Table 1:** Effectiveness of La+3 doping on the lattice parameter, crystallite size, actual (X-ray) density, Bulk density, porosity of (Ni0.4 5 Cu0.20Zn0.45) LaxFe2–xO4 system

| Sample | X concentrations | Lattice Constant (a) | DSh (nm) | DW-H (nm) | \(\rho_{x-ray}\) (g/cm\(^3\)) | \(\rho\) (g/cm\(^3\)) | Porosity % |
|--------|------------------|----------------------|---------|----------|----------------------------|----------------|------------|
| C0     | 0                | 8.353                | 29.50   | 5.43     | 3.56                       | 34.39          |
| C1     | 0.025            | 8.3771               | 29.50   | 5.43     | 3.67                       | 34.39          |
| C2     | 0.050            | 8.3732               | 33.81   | 5.51     | 3.80                       | 31.02          |
| C3     | 0.075            | 8.3745               | 33.81   | 5.51     | 3.80                       | 31.02          |
3.2 SEM Analysis:
The SEM images of various compositions of NiCuZnLa ferrites were shown in the 'figure (3)'. The SEM images reveal that the particles are spherical in shape and are agglomerated in nature. Figure (4) shows the EDX images of all (Ni0.35 Cu0.20Zn0.45) LaxFe2−xO4 ferrite nanoparticles calcined at 900 °C. The characteristic peaks of Ni, Cu, Zn, La, Fe and O elements were observed in EDX spectra.
Figure 4. EDX pattern (Ni0.35 Cu0.20Zn0.45) LaxFe2−xO4 ferrite nanoparticles with (A) x = 0.00, (B) x = 0.075.

3.3 Electrical Properties:
The electrical properties of La doped NiCuZn ferrite (Ni0.35Cu0.20Zn0.45Fe2−xO4) with (X=0.0, 0.025, 0.05 and 0.075) of Lanthanum additions include the A.c and D. c conductivity, dielectric properties.

3.4 Dielectric properties:
With the following equation, dielectric constant real part was detailed [18],

\[ \varepsilon_r' = \frac{C \cdot t}{\varepsilon_0 \cdot A} \]  

where C = the capacitance measured value, d = the thickness in centimeters, A = the surface area in cm², \( \varepsilon_0 \) = air dielectric permittivity (8.854×10⁻¹⁴ F/cm). The dielectric imaginary part loss \( \varepsilon'' \) can be shown as below [18],

\[ \varepsilon'' = \tan \delta \cdot \varepsilon'_r \] 

'Figures(5)' and (6) show the dependence of the real and imaginary part of dielectric constant \( \varepsilon'_r \) and \( \varepsilon'' \), for bulk (Ni0.35 Cu0.20Zn0.45) LaxFe2−xO4 on the frequency \( \omega \), for different lanthanum doping contents. The real and imaginary parts of dielectric constant for all samples decrease with increasing of frequency. This behavior agrees well with Debby's type relaxation process. The real and imaginary parts of dielectric constant reach a constant value for all the samples above certain greater frequency, this agrees with the result of references [19]. It can be observed from Figures 4 that the imaginary parts of dielectric constant \( \varepsilon'' \), increases with frequency.
Figure 5. Real part variation of $(\varepsilon_r')$ of dielectric constant with frequency for $(\text{Ni}_{0.35}\text{Cu}_{0.20}\text{Zn}_{0.45})\text{LaxFe}_{2-x}\text{O}_4$ at different La contents.

Figure 6. Variation of imaginary part $(\varepsilon_r'')$ of dielectric constant with frequency for at $(\text{Ni}_{0.35}\text{Cu}_{0.20}\text{Zn}_{0.45})\text{LaxFe}_{2-x}\text{O}_4$ different La contents.

3.5. A.C. conductivity:
The A.C. conductivity was evaluated using the relation [18],

$$\sigma_{a.c} = 2\pi f \varepsilon_0 \varepsilon_r \tan \delta$$

(9)

Figure (7) shows the ac conductivity differences with frequency (50Hz-1MHz). The ac conductivity increases with increasing frequency for all specimens, which is the normal behavior of ferrites this agrees with the result of references [20].
Figure 7. A.C electrical conductivity as a function of frequency for with (Ni0.35 Cu0.20Zn0.45) LaxFe2–xO4 different contents of La.

3.6. D.C conductivity:
In the following equation D.C conductivity can be calculated:

\[
\sigma_{D.C} = \frac{d}{A R}
\]

Where \( R \) is the resistance \( A \) (m2) it represents the area of the pole, \( d \) (m) is the thickness of pellet. From table (2) obtained that dc conductivity decrease with increasing \( (La+3) \) content.

| Concentration (X) | \( \sigma_{D.C} \times 10^{-19} \) (\( \Omega \).cm) |
|-------------------|---------------------|
| 0.00              | 2.51                |
| 0.025             | 2.32                |
| 0.050             | 2.41                |
| 0.075             | 2.43                |

3.7. Magnetic properties:
The magnetic examinations results displayed that the \( (X=0.05) \) rate with chemical formulation \( (Ni0.35Cu0.2Zn0.45 LaxFe2-XO4) \) own a considerable magnetic features in comparing with other samples due to its best hysteresis circuit in order that it can realize the conditions of utilizing it as a cores in transducers and electrical engines.
Figure 8. Room temperature hysteresis curves of (Ni0.35Cu0.2Zn0.45 LaxFe2-XO4) samples
4. Conclusions
The (Ni0.35 Cu0.20Zn0.4 5) LaxFe2−xO4 where (x= 0.0, 0.025, 0.050 and 0.075) Nano ferrites were all set by Sol-Gel technique. (XRD) studies clearly showed formations of the crystalline structure of (Ni0.35 Cu0.20Zn0.45) LaxFe2−xO4 is cubic spinal stricture phase ferrite and The Average crystallite size (D) was calculated as (27-33nm) using Williamson’s Hall and Debary -sphere equation, the It was found out that lattice parameter increases with increasing lanthanum content. Whereas porosity decreases with increasing lanthanum content. The veritable and fictional part of dielectric constant decreases with increasing of frequency, whilst the A.C electrical conductivity can increase with frequency increasing .and D.C conductivity decreases with increasing lanthanum content. The magnetic examination results presented that the (X=0.05) rate has a considerable magnetic properties in comparing with other samples because of its best hysteresis loop so that it can realize the conditions of utilizing it, as the cores in transducers and electrical motors.

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