Synthesis and characterization of non-stoichiometric $\text{Li}_{1.1}\text{Co}_{0.3}\text{Fe}_{2.1}\text{O}_4$ ferrite nanoparticles for humidity sensors

Mahmoud A. Ateia$^1$ · Ebtesam E. Ateia$^1$ · Mohamed Mosry$^{3,4}$ · M. M. Arman$^{1,2}$

Received: 7 July 2022 / Accepted: 5 September 2022 / Published online: 15 September 2022
© The Author(s) 2022

Abstract
A humidity sensor plays a crucial role in determining the efficiency of materials and the precision of apparatuses. To measure and control humidity, a non-stoichiometric $\text{Li}_{1.1}\text{Co}_{0.3}\text{Fe}_{2.1}\text{O}_4$ mesopore sensor is synthesized by a modified citrate auto combustion technique. The XRD study confirms that prepared nanoparticles are cubic spinel structures having an $\text{Fd}3\text{m}$ space group. The crystallite size is approximately 36 nm. Thermal analysis measurements show that samples become thermally stable at a temperature of 600 °C. Additionally, the kinetic studies of the prepared samples are calculated via a pseudo-first-order kinetic model. The temperature dependence of AC conductivity is found to increase with increasing temperature. These observations are explained in various models. The resistivity mechanism of humidity sensors is studied via complex impedance spectroscopy (CIS). Its impedance data are fitted to a corresponding circuit, to achieve a simulation of the sample under study. This fitting is detected by the Nyquist plot (Cole–Cole). The obtained data confirm that the studied samples are very sensitive to humidity and can be commercially used as a humidity sensing element.

* Ebtesam E. Ateia
  ebtesam@sci.cu.edu.eg; drebtesam2000@yahoo.com

1 Physics Department, Faculty of Science, Cairo University, Giza, Egypt
2 Academy of Scientific Research and Technology (ASRT), Giza, Egypt
3 Building Physics and Environment Institute, Housing & Building National Research Center (HBRC), Dokki 12311, Giza, Egypt
4 Nanotechnology Research Centre (NTRC), The British University in Egypt (BUE), Suez Desert Road, El-Sherouk City 11837, Cairo, Egypt
Keywords Humidity · Nyquist plot · Hopping charge carrier · Spinel nanoparticles

1 Introduction

Precision humidity measurement in the surrounding environment has acquired the curiosity of the scientific community because it has a direct impact on many industries and living organisms [1]. Impedance-based humidity sensors have been proposed using nanostructured metal oxides, ceramics, and polymers. Ceramics and polymers have been suggested as the best candidates for humidity sensors because no expensive noble metal catalyst or complicated synthesizing procedures or treatments are required to achieve moderate sensor performance [2]. The efficiency of the humidity sensors depends on several fascinating factors such as wide span of operating range, fast recovery, and response, promoted sensitivity, stability over long span periods, and durability [3, 4]. Humidity sensors are usually designed and constructed by depositing the sensing materials between two conductive electrodes, where the adsorbed water molecules cause a change in the physical properties of the sensing material [5]. Different configurations of humidity sensors have been proposed and constructed, such as quartz crystal microbalance (QCM), surface acoustic waves (SAW), capacitive, field-effect transistor (FET), resistive, and impedance. The resistive and impedance types are attractive as they are easily fabricated at low cost, have good linearity, and have high sensitivity [6, 7]. Spinel ferrite nanoparticles can be used as humidity sensors due to their high porosity, large surface/volume ratio [8].

Ferrite is an important material whose structure and physical properties are very favorable on a nanometric scale [9]. Among ferrite nanoparticles, lithium ferrite is a class of soft spinel ferrite materials having a square hysteresis loop, excellent dielectric properties, a high Curie temperature, and high saturation magnetization [10]. Besides the mentioned
properties, lithium ferrite is a significant transition metal spinel oxide with the advantages of low price, environmental friendliness, and ease of manufacture [11].

It plays a crucial role as a functional material for different applications such as lithium-ion batteries, electrochromic displays [12] storage devices [13], and sensors [14] [15]. For the synthesis of ferrites, many methods have been proposed and investigated, including high-temperature solid-state reaction [16], co-precipitation, hydrothermal [17], sol–gel [18], high-energy ball mill, and auto combustion [19]. Among all the mentioned methods, auto combustion has the advantages of simplicity, low cost, fast, and additionally, no need for high temperatures [10, 20].

The Li ferrite nanoparticles are indexed according to the space group Fd3m and can be characterized as (A)[B2]O4. A and B represent the tetrahedral and octahedral sites, respectively [21].

The effect of cation substitutions on the physical properties of Li nano ferrites has been examined by many researchers [22, 23]. The reversible loss of lithium and oxygen during the sintering process is the main issue that restricts the synthesizing procedure of the lithium (Li) ferrites. Consequently, Li ferrite is often doped with other cations to adjust its physical properties [24].

The nano ferrite is categorized as a high resistivity material. The increase in surrounding humidity reduces the resistivity of the ferrite nanoparticles. The surrounding humidity can change the resistivity of the ferrite by nearly three orders of magnitude. Generally, the humidity is specified as relative humidity (RH) which signifies the amount of water vapors in the air at a specified temperature. According to a thorough review of the literature, the vast majority of sensors are based on ferrite nanoparticles [25].

The main challenge of this study is to advance ferrite nanoparticles with high quality, and low cost. Through this study, the structural, morphological, thermal, and electrical properties of the Li1.1Co0.3Fe2.1O4 ferrite nanoparticles were elucidated. The structural parameters lattice parameter, the X-ray density (D_X), experimental density (D_experimental), and porosity (P) were calculated. A detailed thermal study was conducted to calculate the half-life (t_1/2), entropy (ΔS°), enthalpy (ΔH°), and Gibbs free energy (ΔG°). The electrical properties of the Li1.1Co0.3Fe2.1O4 nanoparticles were studied at different testing frequencies and different temperatures. The humidity sensing performance of the prepared ferrite was evaluated over a wide span of relative humidity at different testing frequencies. Finally, the humidity sensing mechanism was clarified using Nyquist complex impedance plots over a frequency ranging from 50 Hz up to 5 MHz and at various humidity levels from 40 up to 90%. The current study offers a good reference point for how to maximize the performance of the examined samples in the HS applications.

2 Experimental work

2.1 Materials and sample preparation:

Iron nitrate Fe(NO₃)₃·9H₂O, cobalt nitrate Co(NO₃)₂·6H₂O, and lithium nitrate La(NO₃)₃ were purchased from Sigma-Aldrich. The citric acid (C₆H₈O₇) was acquired from ACROS Organics. As reported previously [26], LiCoFeO nanoparticles were prepared by mixing non-stoichiometric proportions of Fe, Co, and Li nitrates with a calculated amount of C₆H₈O₇ by the citrate auto combustion technique. The ammonia solution was used as a fuel and was added drop by drop to the metal solution to adjust the pH value to 7. The sample was first heated at 80 °C for 60 min with stirring, and then heated at 200 °C till the final product became a fluffy powder. The sample was grinded using an agate mortar for 120 min. The obtained power was calcinated at 600 °C using a rate of 4 °C/min and grinded again for 30 min. Figure 1 illustrates the flowchart for the preparation method of Li1.1Co0.3Fe2.1O4.

Fig. 1 Flowchart for the preparation technique of Li1.1Co0.3Fe2.1O4
2.2 Sensor fabrication and evaluations

The transparent Fluorine doped Tin Oxide (FTO) coated glass substrate has been cleaned to be utilized for sensor fabrication. The electrical contacts were made by connecting two copper foils with conductive adhesive onto the FTO substrate. In brief, a proper amount of sensing material (Li$_{1.1}$Co$_{0.3}$Fe$_{2.1}$O$_4$) has been grinded carefully in an agate mortar for 10 min, then mixed with a suitable amount of distilled water and grinded again for an additional 10 min to form a paste. The slurry was poured on the surface of the pre-cleaned FTO substrate and dried at 60 °C for 12 h. It was conditioned at 90% RH and AC voltage (1 V, 1 kHz) for 24 h to enhance its stability. The behavior and performance of the sensor were evaluated in a homemade humidity-controlled testing chamber as shown in Fig. 2.

The humidity sensor performance was evaluated in a custom-made humidity chamber with a controlled RH value. A commercially available TSI-IAQ thermohygrometer and a 241 PG ultrasonic particle generator were used to measure the RH value and to generate the required level of humidity inside the testing chamber, respectively. The sensor response was measured using an LCR meter (HIOKI 3532-50) with an applied voltage of 1 V-AC and a measurement frequency from 100 to 100 kHz in the range of RH from 40 to 90%.

The humidity controller is connected automatically with the ultrasonic humidifier, and it was adjusted to a specific value of relative humidity. The humidity will enter the closed chamber until it reaches the specific value. Simultaneously, the sensor of the humidity controller will sense it at that moment, the humidifier will be off and the measurements will be done [27].

2.3 Characterization of ferrite nanoparticles

The X-ray diffraction (XRD) pattern of ferrite powder nanoparticles was obtained by an X-ray diffractometer (Xpert PRO MPD) using CuKα radiation. The shape and size distribution of the nanoparticles were investigated using a field emission scanning electron microscope (FESEM, model Quanta 250). STD Q-600 (TGA/DTA) with a heating rate of 20 °C/min in the temperature range of 25–1000 °C under nitrogen atmosphere was used to analyze the phase decomposition and thermal stability of the samples.

In addition, the thermodynamic parameters were determined using the 1st order reaction rate equation as given in the following relation [28]:

\[
\frac{dx}{dt} = k(1 - x) \tag{1}
\]

\[
x = \frac{w_i - w_t}{w_i - w_f} \tag{2}
\]

where \( x \) is the fracture of a sample decomposed at time \( t \), \( k \) is the rate constant of reaction, \( w_i \) is the initial weight, \( w_f \) is the final weight, and \( w_t \) is the weight of the sample at a particular time \( t \).

3 Results and discussion

3.1 The X-ray diffraction (XRD)

Figure 3. illustrates the XRD pattern of the Li$_{1.1}$Co$_{0.3}$Fe$_{2.1}$O$_4$ sample powder. The diffraction pattern exhibited diffraction peaks at 18.43°, 30.37°, 37.53°, 43.67°, 53.95°, 57.43°, and...
63.1° correspondence to (111), (220), (311), (222), (400), (422), (511), and (440) diffraction plans respectively and coincidence with JCPDS card 04-022-8066. No additional peaks were detected in the pattern, signifying that Li$_{1.1}$Co$_{0.3}$Fe$_{2.1}$O$_4$ nanoparticles are completely formed with high purity. The formation of a single-phase cubic spinel structure with a space group (Fd-3 m) is ratified. The average crystallite size is calculated based on the Debye–Scherer’s relation as mentioned in the previous work [29–31].

The value of the lattice parameter ($a_{exp}$) is estimated using the following relation [32]

$$a_{exp} = d\sqrt{h^2 + k^2 + l^2}$$  \hspace{1cm} (3)

where $d$ is the $d$-spacing and $(hkl)$ are the Miller indices of the planes associated with characteristic peaks. The X-ray density ($d_x$), experimental density ($d_{exp}$), and porosity ($P$), for Li$_{1.1}$Co$_{0.3}$Fe$_{2.1}$O$_4$ are demonstrated using Eqs. 4, 5 and 6 respectively [33]. The calculated data are illustrated in Table 1.

$$d_x = \frac{ZM}{a_{exp}^3 N_A}$$  \hspace{1cm} (4)

$$d_B = \frac{m}{\pi r^2 t}$$  \hspace{1cm} (5)

Table 1 The experimental lattice constant ($a_{exp}$), the theoretical density ($d_x$), experimental density ($d_{exp}$), porosity ($P$) and crystallite size ($D$) of the investigated sample. 

| Sample          | $a_{exp}$ ($\text{Å}$) | $d_x$ ($\text{g/cm}^3$) | $d_{exp}$ ($\text{g/cm}^3$) | $P$ (%) | $D$ (nm) |
|-----------------|------------------------|-------------------------|-----------------------------|---------|----------|
| Li$_{1.1}$Co$_{0.3}$Fe$_{2.1}$O$_4$ | 8.324                  | 4.758                   | 2.528                       | 46.86   | 36       |

$P(\%) = \left(1 - \frac{d_B}{d_x}\right) \times 100$  \hspace{1cm} (6)

where $Z$ is the number of molecules per unit cell (for spinel ferrites $Z = 8$), $M$ is the molecular weight of the sample (g/mole), $N_A$ is the Avogadro's number ($6.023 \times 10^{23}$ atom/mole), and $m$, $r$, and $t$ are the mass, radius, and thickness ($t = 3.47$ mm), respectively, of each pellet of Li$_{1.1}$Co$_{0.3}$Fe$_{2.1}$O$_4$ nano ferrite sample. All the structural related parameters are presented in Table 1.

### 3.2 Field emission scanning electron microscope (FESEM)

The FESEM images of the investigated sample are presented in Fig. 4a, b. The FE-SME images of Li$_{1.1}$Co$_{0.3}$Fe$_{2.1}$O$_4$ nanoparticles demonstrate a sponge and fluffy like structure. At low magnification (Fig. 4a) the Li$_{1.1}$Co$_{0.3}$Fe$_{2.1}$O$_4$ seems to be agglomerated without any obvious details regarding the grain size, structure, or orientation. At high magnification (Fig. 4b) the particles appear as sponges with noticeable agglomeration. The grains, with their porous nature and rocky-like shape clearly appeared. The appearance of pores can be attributed to the escape of gasses during the combustion process. The same behavior was attained for copper nano ferrites [34].

The FESEM images show that some of the particles combined with each other to form clusters and leave some spaces as pores. These pores serve as humidity or gas adsorption sites, as will be discussed later. The detected porosity from XRD agrees with the FESEM images. This morphology of Li$_{1.1}$Co$_{0.3}$Fe$_{2.1}$O$_4$ is highly recommended for humidity sensor applications.

![FESEM images of Li$_{1.1}$Co$_{0.3}$Fe$_{2.1}$O$_4$ sample](image.png)
3.3 Thermal analysis

TGA-DTA curves of the Li$_{1.1}$Co$_{0.3}$Fe$_{2.1}$O$_4$ ferrite in the temperature range 25–1000 °C under an N$_2$ atmosphere with a heating rate of 20 °C min$^{-1}$ are shown in Fig. 5a. The TGA thermogram of the sample exhibits three weight losses in the temperature ranges of (1) 30–170 °C, (2) 170–430 °C, and (3) 450–800 °C. The first stage of weight loss (WL) corresponds to 0.9% due to the evaporation of residual water during the preparation technique. Similarly, the DTA curve of the Li$_{1.1}$Co$_{0.3}$Fe$_{2.1}$O$_4$ represents an exothermic peak around 130 °C due to water evaporation.

In the second stage, WL $\approx$ (1.62%) corresponds to the volatilization of the organic solvents and represents an exothermic peak (DTG) around 400 °C. The third step of the TGA plot is after 600 °C where the WL is in the range of (0.58%). This WL may be due to improving the crystallization process of the materials.

The TGA thermogram shows no further WL above 650 °C, confirming the formation of the stable Li$_{1.1}$Co$_{0.3}$Fe$_{2.1}$O$_4$ nano ferrite sample. The exothermic peaks in the DTA curve are consistent with the change regions in the TGA pattern. The kinetic study of the prepared sample is calculated via a pseudo-first-order kinetic model. The rate constant ($k$) can be obtained from the slope of the linear plot of ln (1 – $x$) against time ($t$) using the next equation [35, 36].

$$\ln(1 - x) = -kt$$

The half-life ($t_{1/2}$) is determined using Eq. (8), and the obtained results are illustrated in Table 2.

$$t_{1/2} = 0.693/k$$

The Coats and Redfern model can be used to detect the kinetics parameters as designated in the following formula [28]:

$$\ln[-ln(1 - x)] = \ln\left(\frac{A T^2}{\beta E_a} - \frac{E_a}{RT}\right)$$

where $A$, $\beta$, and $R$ are the pre-exponential parameter, the heating rate (20 °C/min), and the universal gas constant (8.3143 Jmol$^{-1}$ K$^{-1}$) respectively. While $E_a$ and $T$ are the activation energy and the temperature ($K$) respectively. The $E_a$ can be calculated by plotting ln [ln (1 – $x$)] versus 1000/T, as shown in Fig. 5c.

In the present case the chemically controlled reaction is predominant as ratified by $E_a$ values (> 25 kJ mol$^{-1}$). Other parameters, such as change of entropy ($\Delta S_o$), enthalpy ($\Delta H_o$), and Gibbs free energy ($\Delta G_o$), are calculated using basic thermodynamic equations [37].

$$\Delta H = E_a - R T_g$$

$$\Delta S = R \ln\left(\frac{A h}{K T_g}\right)$$

$$\Delta G = \Delta H - T_g \Delta S$$
where $h$ and $K$ are the Blank constant and Boltzmann constant, respectively. The results for each stage are tabulated in Table 2. The positive value of $\Delta H'$ designates the input heat energy which is required for the reactants. The degree of disturbance of the system can be identified by $\Delta S$. The negative value of $\Delta S'$ specifies that the transition state orientation is higher compared to the reactants in the ground state. Additionally, it signifies that the Li$_2$O + Co O + Fe O join together to form LiCoFeO which is more organized and stable compared to the ground state and subsequently decreases the randomness of the system. The $\Delta G$ gives an idea of either the non-spontaneity or spontaneity of the reaction depending on the $+$ ve or $-$ ve values of $\Delta G'$. In the present study, $+$ ve values of $\Delta G$ indicate the non-spontaneous nature of the process.

### 3.4 Electrical properties

The electrical properties of doped nano ferrites are the most important characteristics, since they have a significant impact on the enhancement of the humidity application. As shown in Fig. 6a, b, the dielectric constant ($\varepsilon'$) gradually increases with increasing temperature and decreases with increasing frequency. In the first region of the temperature, the thermal energy provided to the system is insufficient to liberate the localized dipoles until $T \approx 550$ K.

In the second region, the thermal energy liberates more localized dipoles, and the field accompanied by the applied frequency aligns them in its direction up to peak $T \approx 650$ K. According to Koop’s’ model, ferrites are comprised of two layers, the first is low resistance grains, and the other is high-resistance grain boundaries.

When the electric field is applied to the investigated sample, electrons accumulate at grain boundaries and hinder electron conduction. Electron hopping occurs primarily between the elements at the B site as Fe$^{2+}$–Fe$^{3+}$ and Co$^{2+}$–Co$^{3+}$ ions in Li$_{1.1}$Co$_{0.3}$Fe$_{2.1}$O$_4$ [38].

The excess of metal ions in Li$_{1.1}$Co$_{0.3}$Fe$_{2.1}$O$_4$ (B cations $> 2$) will greatly increase the probability of electron hopping between Fe$^{2+}$/Fe$^{3+}$, and Co$^{2+}$/Co$^{3+}$ ions. This hopping causes local displacement in the external field direction, producing a change in polarization as well as $\varepsilon'$. The decrease in $\varepsilon'$ after the peak is due to an increase in the lattice vibration, which causes scattering of charge carriers as well as disordering of the dipoles, with the result that $\varepsilon'$ decreases. As shown from the figures, the dielectric transition point shifts slightly to a lower value with increasing frequency which means that the ferrimagnetic region decreases and the paramagnetic region (disordered state) increases. This can be attributed to the disturbing effect of an oscillating electric field as its frequency increases.

The drop in $\varepsilon'$ with increasing frequency is due to the fast alternation of the field accompanied by the applied frequency, where the alternation of the dipoles increases as well as the friction between them. The quantity of heat dissipated in the entire volume of the sample increases, and the aligned dipoles will be disturbed with the result of decreasing $\varepsilon'$.

The relation of $\ln \sigma$ ($\sigma$: conductivity) versus $1000/T$ at various frequencies is shown in Fig. 7. This plot is fitted for each region to the linear regression line with the appropriate parameter $R^2 \approx 0.99$.

Furthermore, it increases with increasing temperature, confirming the semiconducting-like behavior. The plot of Fig. 7 can be divided into three numerous temperature regions corresponding to three numerous conduction mechanisms.

The first is the hopping mechanism that appears below the transition temperature $T_c$, where the $\sigma$ is frequency and temperature-dependent. The second mechanism above $T_c$ is temperature-dependent and frequency-independent. It is
related to the drift mobility of the thermally activated electrons and not to the thermal creation of the charge carriers.

In the third region, from 300 to 386 K, the $\sigma$ slightly decreases with increasing temperature giving rise to a metallic-like behavior. The $T_c$ of the investigated sample occurs at $\approx 605$ K.

The activation energies (AE) at different frequencies are estimated from the Arrhenius relation [39] and given in Table 3. The AE for electron hopping (Fe$^{2+}$/Fe$^{3+}$) is of the order of 0.1 eV as estimated by Ateia et al. [40, 41]. However, the double exchange (DE) electron hopping as Fe$^{2+}$ + Co$^{3+}$ ⇔ Fe$^{3+}$ + Co$^{2+}$ requires more energy for the conduction, and then the AE would naturally be considerably larger. Accordingly, in the present case, the obtained AE in the range of 0.2–0.3 eV suggests that the DE interaction process is more predominant. The obtained values of AE agree well with those reported for DE electron hopping (0.25 eV) [42].

Figure 7b illustrates the relation of $\ln \sigma$ ($\sigma$: conductivity) and $\ln \omega$ ($\omega$: angular frequency) for the Li$_{1.1}$Co$_{0.3}$Fe$_{2.1}$O$_4$ as a function of the absolute temperature. The $\sigma_{ac}$ obeyed the power law that was discussed previously [42].

$$\sigma_{ac}(\omega) = B\omega^S$$  \hspace{1cm} (13)

where $\sigma_{ac}$ is the ac conductivity, $\omega = 2\pi f$ denotes the angular frequency, $B$ denotes a temperature-dependent constant and $S$ denotes the frequency-dependent exponent. The slope of lines represents the value of the exponent factor ($S$). The experimental value of the slope $S$ attained for Li$_{1.1}$Co$_{0.3}$Fe$_{2.1}$O$_4$ is of the order of 0.57. The attained value agrees well with the values (0.6–1.0) found for the hopping mechanism in most transition metal oxide materials [43].

3.5 The molar magnetic susceptibility ($\chi_M$)

The thermal variation of $\chi_M$ is illustrated in Fig. 8a. Ferrimagnetic behavior is the main trend over a wide temperature region. The data reveal the slow decrease in $\chi_M$ with increasing temperature. The thermal energy given to the sample is insufficient to overcome the magnetic field effect. At high temperatures in the paramagnetic region (above $T_c$) the thermal energy due to heating increases the lattice vibration as well as the spin randomization. In the case study, the disturbance in the system increases leading to a drop in the magneto crystalline anisotropy and overcoming the field effect. The $T_c$ is calculated from $d\chi_M/dT$ as an accurate value. It is demonstrated in the inset of the figure.

The obtained data obey the well-known Curie–Weiss law where $1/\chi_M$ varies linearly with temperature in the paramagnetic region, as shown in Fig. 8b, c. The values of the Curie constant ($C$), Curie–Weiss constant ($\theta$), and the effective magnetic moment ($\mu_{eff}$) are calculated from the $1/\chi_M$ with $T$ and reported in Table 4 using the following equations [44–46].

Table 3  The activation energies for Li$_{1.1}$Co$_{0.3}$Fe$_{2.1}$O$_4$

| Frequency (kHz) | 50   | 90   | 300  | 500  | 900  | 1000 |
|----------------|------|------|------|------|------|------|
| Activation energy |      |      |      |      |      |      |
| $\sigma_1$ | 0.25 | 0.21 | 0.26 | 0.29 | 0.30 | 0.29 |
| $\sigma_{II}$ | 0.98 | 0.93 | 0.82 | 0.77 | 0.63 | 0.67 |
Humidity sensing studies

The porosity is an essential parameter for a humidity sensor (HS) and it is a significant feature of nano ferrite. The variation of impedance during exposure to humidity is a basic requirement for the humidity sensor. This disparity depends on the band gaps, surface morphology, size, diffusion rate of gas, and specific surface area (SSA) of the used magnetic materials [47].

As shown in Fig. 9a, b, the variation of impedance in the frequency range of 100–100 kHz as a function of controlled humidity from 20–90 RH% is demonstrated. It is obvious that the impedance experiences no change up to 40% RH, then decreases with increasing testing frequency. At higher frequencies, the impedance variation is insignificant due to the inability of a water molecule to be polarized at higher frequencies [48].

The ultimate variation of the impedance is accomplished at 100 Hz. Consequently, the humidity sensing performance of the Li$_{1.1}$Co$_{0.3}$Fe$_{2.1}$O$_4$ nanocomposite is further evaluated

---

**Table 4** The magnetic constants: Weiss constant ($\theta$), the Curie constant ($C$), effective magnetic moment ($\mu_{\text{eff}}$), Curie temperature ($T_c$) from the Curie–Weiss law

| Sample             | $H$ (Oe) | $C$ (emu/mole.K/g) | $\mu_{\text{eff}}$ (B.M.) | $T_c$ (K) | $\theta$ (K) |
|--------------------|----------|--------------------|---------------------------|-----------|--------------|
| Li$_{1.1}$Co$_{0.3}$Fe$_{2.1}$O$_4$ | 1010     | 20.023             | 12.666                    | 718       | 690          |
|                    | 1340     | 17.313             | 11.775                    | 715       | 688          |
|                    | 1660     | 16.742             | 11.579                    | 713       | 675          |

\[
C = \frac{1}{\text{slope}} \tag{14}
\]

\[
\mu_{\text{eff}} = 2.83 \sqrt{C} \tag{15}
\]
at 100 Hz. Moreover, a humidity level lower than 40% is not recommended to be used as humidity sensing for the studied sample. This is clarified by the physical/chemical adsorption of a water molecule on the surface of the sensor. The response of the humidity sensor exhibited an exponential decrease with an increase in the humidity level, as represented in Fig. 9b. The impedance variation is fitted by an exponential function expressed by the following equation:

\[ Y = A_1 e^{(-\frac{x}{t_1})} + y_0 \]  

(16)

where \( A_1, t_1, \) and \( y_0 \) are constants.

The humidity sensing characteristic of the nanoparticles is elucidated through three sequential processes involving chemisorption, physisorption, and capillary condensation. Initially, at low RH values (less than 40%), water molecules (WMs) are chemically adsorbed on the surface of the sensing materials via double hydrogen bonds and self-ionized to form \( H^+ \) and \( OH^- \). Because of the nature of the double hydrogen bonds, the proton needs more energy to move freely between neighboring \( OH^- \) groups. At this stage, the \( OH^- \) groups are hindered, thereby no change in impedance is detected. On the other hand, by increasing the RH level, the second layer of WM starts to be physically adsorbed on the active sites of the surface of the sensor via a single hydrogen bond. Due to the formation of a single hydrogen bond, the WMs become mobile and behave like those in the bulk liquid. In this mode, the amount of ionized WMs generates a large number of hydronium ions (\( H_3O^+ \)) which act as charge carriers. Hence, the required energy for hopping of the generated protons is decreased, enabling them for hopping between adjacent WM, thereby decreasing the sensor impedance. This mechanism is known as the chain reaction or Grotthuss mechanism [49].

\[ \text{H}_2\text{O} \leftrightarrow \text{H}^+ + \text{OH}^- \]  

(17)

\[ \text{H}_2\text{O} + \text{H}^+ \leftrightarrow \text{H}_3\text{O}^+ \]  

(18)

With further increase in RH level, multiple physisorbed layers are stacked up and the WMs condenses in the pores causing a further decrease in sensor impedance. The described mechanism is illustrated in Fig. 10.

Hysteresis is one of the essential parameters required to evaluate the reproducibility of the humidity sensor. The manufactured sensor is subjected to a controlled humidification/desiccation regime from 40 up to 90% RH as depicted in Fig. 11. It is ratified that the desorption process is commonly slower than the adsorption process, hence the variation of the impedance is slightly lower during the desorption compared to that in the adsorption process. As demonstrated in Fig. 11, the sensor exhibits less hysteresis, and such a humidity sensor is a favor to be integrated into real-time humidity monitoring devices. More importantly, as shown in Fig. 9b, the response of the \( \text{Li}_{1.1}\text{Co}_{0.3}\text{Fe}_{2.1}\text{O}_4 \) nanocomposite increases exponentially with increasing RH value from 40 to 90%.

The conductivity mechanism of the humidity sensor is studied via Complex Impedance Spectroscopy (CIS) [50]. The Nyquist complex impedance plots for \( \text{Li}_{1.1}\text{Co}_{0.3}\text{Fe}_{2.1}\text{O}_4 \) are estimated over a frequency ranging from 50 Hz up to 5 MHz at various humidity levels from 40 up to 90% as shown in Fig. 12a–d. Under low humidity circumstances, only a nearly straight line is established. A semicircle starts to appear in the humidity level (60—70%).

---

**Fig. 10** The mechanism of \( \text{Li}_{1.1}\text{Co}_{0.3}\text{Fe}_{2.1}\text{O}_4 \) composite as humidity sensing behavior
With a further increment in the RH level, the curvature of the semicircle shrinks due to the interaction between WM and the surface of the sensing material. Finally, at a higher level of humidification (80–90% RH) a semicircle is generated in addition to a straight line in the low-frequency region.

The difference in impedance curves can be associated with the numerous adsorption mechanisms. The intrinsic impedance of the sensor can be identified by the semicircle in the CIS curves. While, the line at low frequency demonstrates the Warburg impedance [51]. A few WM are adsorbed on the surface of the sensor under low humidity situations, and a semicircle or incomplete semicircle occurs in the CIS plot, to curb the movement of the charge carrier. Further increase in humidity level, the Warburg impedance is prevalent, which indicates that a continuous water layer is formed on the surface of the sensor and hence the ionic conduction is initiated. Additionally, the CIS of the examined sample depends on an idealized circuit model. The impedance data are superimposed on an equivalent circuit to achieve a simulation of the prepared sensor. The Nyquist plot (Cole–Cole) can be utilized to identify the data. The equivalent circuit is demonstrated in the inset of Fig. 12c, d. The electric circuit elements have been attained using Z-view software.

![Fig. 11](image) The hysteresis loop for adsorption and desorption process at 100 Hz and 300 K

![Fig. 12](image) a The Nyquist complex impedance curves for Li_{1.1}Co_{0.3}Fe_{2.1}O_{4} at RH (40:50)%.

b at RH (60:70)%. c at RH (80)%. d at RH (90)% at room temperature
Finally, the results clarify that Li$_{1.1}$Co$_{0.3}$Fe$_{2.1}$O$_4$ nano ferrites contain two phases; the grain and the grain boundary. Also, approve that the clarification of the behavior of dielectric parameters and conductivity is on the correct track.

4 Conclusion

The ferrite nano particles Li$_{1.1}$Co$_{0.3}$Fe$_{2.1}$O$_4$ was synthesized in a single-phase cubic spinel structure using the citrate auto combustion technique. The FESEM images illustrated the porous nature and rocky-like shape of the sample. The main conduction mechanism is the electron hopping between the elements at the B site, as Fe$^{2+}$–Fe$^{3+}$, and Co$^{2+}$–Co$^{3+}$ ions. The maximum impedance value is achieved at 100 Hz; therefore, the humidity sensing behavior of Li$_{1.1}$Co$_{0.3}$Fe$_{2.1}$O$_4$ is evaluated at 100 Hz. The humidity sensing behavior of the nanoparticles has two mechanisms; the chemisorption at low RH values and the physisorption at high RH values. The increase in the RH level decreases the curvature of the semicircle due to the interaction between water molecules and the surface of the sensing material.

Acknowledgements This paper is supported financially by the Academy of Scientific Research and Technology (ASRT), Egypt, under initiatives of Science Up Faculty of Science (Grant No. 6722).

Author’s contribution EEA: experimentation, written the original manuscript, reviewing and editing the final manuscript, supervision. MAA: material preparation, data collection and analysis, Optimum selection of material parameters, experimentation, validation and visualization. MMM: experimentation, written the original manuscript, and editing the final manuscript. MMA: conceptualization, investigation; experimentation, review and editing.

Funding Open access funding provided by The Science, Technology & Innovation Funding Authority (STDF) in cooperation with The Egyptian Knowledge Bank (EKB). This research was funded by Academy of Scientific Research & Technology (No. 6722).

Availability of data and material Not applicable.

Code availability Not applicable.

Declarations

Conflict of interest The authors declare that they have no conflict of interest.

Ethics approval Not applicable.

Open Access This article is licensed under a Creative Commons Attribution 4.0 International License, which permits use, sharing, adaptation, distribution and reproduction in any medium or format, as long as you give appropriate credit to the original author(s) and the source, provide a link to the Creative Commons licence, and indicate if changes were made. The images or other third party material in this article are included in the article’s Creative Commons licence, unless indicated otherwise in a credit line to the material. If material is not included in the article’s Creative Commons licence and your intended use is not permitted by statutory regulation or exceeds the permitted use, you will need to obtain permission directly from the copyright holder. To view a copy of this licence, visit http://creativecommons.org/licenses/by/4.0/.

References:

1. S.N. Patil, A.M. Pawar, S.K. Tilekar, B.P. Ladgaonkar, Investigation of magnesium substituted nanoparticle zinc ferrites for relative humidity sensors. Sens. Actuators, A 244, 35–43 (2016). https://doi.org/10.1016/j.sna.2016.04.019
2. V. Manikandan et al., Rapid humidity sensing activities of lithium-substituted copper-ferrite (Li–CuFe$_2$O$_4$) thin films. Mater. Chem. Phys. 229, 448–452 (2019). https://doi.org/10.1016/j.matchemphys.2019.03.043
3. N.A. Roslan et al., Enhancing the performance of vanadyl phthalocyanine-based humidity sensor by varying the thickness. Sens. Actuators, B: Chem. 279(2018), 148–156 (2019)
4. H. Moustafa, M. Morsy, M.A. Ateia, F.M. Abdel-Haleem, Ultrafast response humidity sensors based on polyvinyl chloride graphene oxide nanocomposites for intelligent food packaging. Sens. Actuators, A 331, 112918 (2021)
5. L. Xu et al., Coolmax/graphene-oxide functionalized textile humidity sensor with ultrafast response for human activities monitoring. Chem. Eng. J. 412, 128639 (2021)
6. S. Yu, H. Zhang, C. Chen, C. Lin, Investigation of humidity sensor based on Au modified ZnO nanosheets via hydrothermal method and first principle. Sens. Actuators, B: Chem. 287, 526–534 (2019)
7. M. Velumani, S.R. Meher, Z.C. Alex, Composite metal oxide thin film based impedometric humidity sensors. Sens. Actuators, B: Chem. 301, 127084 (2019)
8. R. Cheruku, G. Govindaraj, L. Vijayan, Super-linear frequency dependence of ac conductivity in nanocrystalline lithium ferrite. Mater. Chem. Phys. 146, 389–398 (2014). https://doi.org/10.1016/j.matchemphys.2014.03.043
9. M.M. Hessien, Synthesis and characterization of lithium ferrite by oxalate precursor route. J. Magn. Magn. Mater. 320(21), 2800–2807 (2008). https://doi.org/10.1016/j.jmmm.2008.06.018
10. M.H. Abdellatif, Fractal growth of ferrite nanoparticles prepared by citrate-gel auto-combustion method. Silicon 10, 1991–1997 (2018)
11. E.E. Ateia, M.A. Ateia, M.G. Fayad, S.I. El-Hout, S.G. Mohamed, M.M. Arman, Synthesis of nanocubic lithium cobalt ferrite toward high-performance lithium-ion battery. Appl. Phys. A 128, 483 (2022)
12. M. Bahgat, F.E. Farghaly, S.A. Basir, O.A. Fouad, Synthesis, characterization and magnetic properties of microcrystalline lithium cobalt ferrite from spent lithium-ion batteries. J. Mater. Process. Technol. 183(1), 117–121 (2007)
13. J.J. William, I.M. Babu, G. Muralidharan, Lithium ferrite (α-LiFe$_5$O$_8$) nanorod based battery-type asymmetric supercapacitor with NiO nanoflakes as the counter electrode. New J. Chem. 43(38), 15375–15388 (2019)
14. V. Manikandan et al., Fabrication and characterization of Ru-doped LiCuFe$_2$O$_4$ nanoparticles and their capacitive and resistive humidity sensor applications. J. Magn. Magn. Mater. 474, 563–569 (2019). https://doi.org/10.1016/j.jmmm.2018.11.072
15. N. Rezlescu, C. Doroftei, E. Rezlescu, P.D. Popa, Sens. Actuators B Chem. 133, 420 (2008). https://doi.org/10.1016/j.snb.2008.02.047
16. B. Mali, K. Ashok, H. Sreemoolanadhan, S. Elizabeth, Tuning of magnetic properties in Cr-doped lithium ferrite. J. Alloys Comp. 911, 165036 (2022). https://doi.org/10.1016/j.jallcom.2022.165036

17. A. Ahnhiyaz, T. Fujiwara, S.W. Song, M. Yoshimura, Low temperature preparation of j- LiFeO2 fine particles by hydrothermal ball milling. Solid State Ionicas 151(1–4), 419–423 (2002)

18. S.S. Teixeira, F. Amaral, M.P.F. Graça, L.C. Costa, Comparison of lithium ferrite powders prepared by sol–gel and solid-state reaction methods. Mater. Sci. Eng., B 255, 114529 (2020). https://doi.org/10.1016/j.mseb.2020.114529

19. B. Randhawa, H. Dosanjh, N. Kumar, Synthesis of lithium ferrite by precursor and combustion methods: a comparative study. J. Radioanal. Nucl. Chem. 274(3), 581–591 (2017). https://doi.org/10.1007/s10904-017-2747-9

20. J.V. Angadi, A.V. Anupama, R. Kumar, H.K. Choudhary, S. Mathur, K.H. Somashekarappa, B. Rudraswamy, B. Sahoo, Composition dependent structural and morphological modifications in nanocrystalline Mn-Zn ferrites induced by high energy gamma-irradiation. Mater. Chem. Phys. 199, 313–321 (2017). https://doi.org/10.1016/j.matchemphys.2017.07.021

21. H.M. Widatallah, C. Johnson, F.J. Berry, E. Jartych, A.M. Gissendanner, B.K. Kuan, Effect of the strong relaxer cobalt on the parallel and perpendicular pumping spin-wave instability threshold of LiTi ferrites. J. Magn. Magn. Mater. 163, 164–172 (1996). https://doi.org/10.1016/0304-8853(96)00306-X

22. G. Mathew, S.N. Swapnw, A.M. John, P.A. Joy, M.R. Ananthaparv, H.M. Somashekarappa, B. Rudraswamy, B. Sahoo, Influence of cobalt substitution on structural, optical, and magnetic properties on heavy metal ions removal from water. J. Mater. Sci.: Mater. Electron. 33, 10806–10818 (2017). https://doi.org/10.1007/s10854-017-6858-X

23. K.H. Mahmoud, M.H. Makled, Infrared spectroscopy and thermal stability studies of natural rubber-barium ferrite composites. Adv. Chem. Eng. Sci. 2, 350–358 (2012)

24. P. Thakur, P. Sharma, J.L. Mattei, P. Queffelec, A.V. Trukhanov, E.E. Ateia, M.A. Ateia, M.M. Arman, Assessing of channel structure and performance of the heterogeneous LaSnO3–TiO2 nanocatalyst with enhanced catalytic activity under visible light. J. Mater. Sci.: Mater. Electron. 28(15), 10806–10818 (2017). https://doi.org/10.1007/s10854-017-6858-X

25. S. Perveen, M.A. Farrukh, Influence of lanthanum precursors on the heterogeneous LaSnO3–TiO2 nanocatalyst with enhanced catalytic activity under visible light. J. Mater. Sci.: Mater. Electron. 28(15), 10806–10818 (2017). https://doi.org/10.1007/s10854-017-6858-X

26. E.E. Ateia, M.K. Abdelmaksoud, H. Ismail, A study of the magnetic properties of GdFe2O4 nanocomposites. J. Mater. Sci.: Mater. Electron. 39, 4180–4190 (2019). https://doi.org/10.1016/j.jsmatselec.2019.07.094

27. E.E. Ateia, M.K. Abdelmaksoud, H. Ismail, A study of the magnetic properties of GdFe2O4 nanocomposites. J. Mater. Sci.: Mater. Electron. 39, 4180–4190 (2019). https://doi.org/10.1016/j.jsmatselec.2019.07.094

28. E.E. Ateia, A.T. Mohamed, Nonstoichiometry and phase stability of Li1.1Co0.3Fe2.1O4 ferrite...
49. P. Chavan, Chemisorption and physisorption of water vapors on the surface of lithium-substituted cobalt ferrite nanoparticles. ACS Omega 6(3), 1953–1959 (2021). https://doi.org/10.1021/acsomega.0c04784

50. T.Ş Kuru, M. Kuru, S. Bağcı, Structural, dielectric and humidity properties of Al–Ni–Zn ferrite prepared by co-precipitation method. J. Alloys Comp. 753, 483–490 (2018). https://doi.org/10.1016/j.jallcom.2018.04.255

51. X. Zhao, X. Chen, X. Yu, X. Ding, X.L. Yu, X.P. Chen, Fast response humidity sensor based on graphene oxide films supported by TiO₂ nanorods. Diam. Relat. Mater. 109, 108031 (2020)

Publisher's Note Springer Nature remains neutral with regard to jurisdictional claims in published maps and institutional affiliations.