Enhancing the Magnetization, Dielectric Loss and Photocatalytic Activity of Co-cu Ferrite Nanoparticles Via the Substitution of Rare Earth Ions

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Research Article

Keywords: CCL, RhB, nanocrystals synthesized, STEM-EDX, anisotropy

Posted Date: August 5th, 2021

DOI: <https://doi.org/10.21203/rs.3.rs-770192/v1>

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Abstract

This study reports the impact of lanthanum substituted Co-Cu ferrite nanoparticles on the RhB dye disposal. Moreover, a complete investigation for the structural, magnetic and optical properties for $\text{Co}_{0.5}\text{Cu}_{0.5}\text{La}_x\text{Fe}_{2-x}\text{O}_4$ (CCL) nanoferrites was executed. These nanocrystals synthesized via a combustion approach with a peculiar lattice parameter behavior; which discussed through three hypotheses. STEM-EDX micrographs of some selective samples confirm the nanocrystalline nature with presence of all constituents' chemical elements CCL nanoferrites. The saturation magnetization of CCL nanoferrites was tuned with La^{3+} ions substitution. Contrary to the expected results, anisotropy constant introduced a decrement behavior with La/Fe substitution process. The microwave frequency (ω_M) values for all CCL nanoparticles are in the range 11.87 GHz–9.46 GHz. The band gap has a peculiar behavior; a red shift and followed by a blue one. Through photodegradation testing, we explicate the RhB degradation mechanisms over our CCL nanoferrites. The nanoferrite $\text{Co}_{0.5}\text{Cu}_{0.5}\text{La}_{0.15}\text{Fe}_{1.85}\text{O}_4$ has a moderate saturation magnetization, highest coercivity, and lowest loss which is a suitable candidate for data recording applications, furthermore can be utilized as a photocatalyst for RhB effluents removal with degradation efficiency 94.50% at 180 min solar radiation.

1. Introduction

In day-to-day life environmental pollution from organic dyes became an intractable problem. Particularly, rhodamine B (RhB) organic dye can be vastly utilized in diverse purposes. Physically, RhB is bright-red in color with molecular formula $\text{C}_{28}\text{H}_{31}\text{ClN}_2\text{O}_3$, molecular weight 479 g/mol and water solubility (8–15 g/L at 20°C). In fact, RhB can cause reliable environmental problems, besides its capability to make skin or eyes irritation [1]. All these factors motivate us to generate effectual and cost-effective removal technique to overcome this environmental threat. Photocatalytic degradation of dyes using spinel ferrite nanoparticles is a salutary and environmentally friendly approach for dyes removal [2]. Recently, researches focus in the field of utilizing spinel ferrites as catalysis due to its moderately narrower band gap (~ 2.0 eV), where can absorb both Vis. and UV radiations [3]. Moreover, the magnetic nature of spinel ferrites empowering its easy separation and retrieval of the ferrite powder again [4]. Kefeni et al., [5] declared that cobalt and copper ferrites (CoFe_2O_4 & CuFe_2O_4) besides their corresponding composites introduce higher photocatalytic performances. Consequently, we got excited to exploit a new nanoferrite containing both cobalt and copper cations ($\text{Co}_{0.5}\text{Cu}_{0.5}\text{Fe}_2\text{O}_4$) which doping with a rare earth element to augment their overall photocatalytic performance. Rather than their catalytic performances, $\text{Co}_{0.5}\text{Cu}_{0.5}\text{Fe}_2\text{O}_4$, also, acquire amazing properties among the reminder ferrite types [6]. Indeed, CoFe_2O_4 is a promising material for diverse implementations based on its highest magneto-crystalline anisotropy ($\sim 3 \times 10^5 \text{ J.m}^{-3}$) [7]. This property make CoFe_2O_4 has a feature suitable for storage devices applications. Basically, the crucial necessity for these magnetic materials utilizing in storage data that it should been have moderate saturation magnetization and high coercivity (H_C), which are satisfied in CoFe_2O_4 nanoparticles [8]. Additionally, CuFe_2O_4 nanoparticles with the Jahn-Teller ion (Cu^{2+}) have ubiquitous

applications; based on their magneto-strictive property for the ferrite material [9]. Hence, in this investigation, by choosing $\text{Co}_{0.5}\text{Cu}_{0.5}\text{Fe}_2\text{O}_4$ nanoferrite to be the pristine sample we can obtain the two features producing high H_C ; higher magneto-crystalline anisotropy (by CoFe_2O_4) besides higher magneto-strictive property (by CuFe_2O_4). Generally, Rare earth elements have auspicious effect on enhancement diverse nanoferrite systems [10–12]. Our research group, in the previous publication, declared that the substitution of lanthanum (La), as a rare earth element, into Zn-Mg ferrite system enhanced its physical properties besides improving its degradation efficiency [13]. So, we are enthused to use La ion to enhance the features of another nanoferrites system as $\text{Co}_{0.5}\text{Cu}_{0.5}\text{La}_x\text{Fe}_{2-x}\text{O}_4$. Thus, by adding La^{3+} ions, it is expected to obtain the following results; (1) moderate value of magnetization, where La^{3+} ions have lower magnetic moment than Fe^{3+} ions; (2) high value of coercivity, where La^{3+} ions will generate spin-orbit coupling between 4f and 3d levels; (3) diminishing the energy gap, by energy levels creation by lanthanum electrons inside band gap, and interns enhance the photocatalytic property. In view of hopeful properties of spinel ferrite nanoparticles, current research investigates structural, magnetoelectric, optical features besides photocatalytic activity of $\text{Co}_{0.5}\text{Cu}_{0.5}\text{La}_x\text{Fe}_{2-x}\text{O}_4$ nanoparticles; which is not investigated until now.

2. Materials And Methods

Pure and La^{3+} subrogated $\text{Co}_{0.5}\text{Cu}_{0.5}\text{Fe}_2\text{O}_4$ nanoferrites were prepared through citrate combustion technique. In this approach metals nitrate; cobalt, copper, iron, lanthanum, with definite amounts, in addition to citric acid and ammonia solution were used. The combustion process of $\text{Co}_{0.5}\text{Cu}_{0.5}\text{La}_x\text{Fe}_{2-x}\text{O}_4$ (CCL); ($0 \leq x \leq 0.15$; step 0.03) ferrite nanoparticles are reported minutely in an earlier publication [14]. The yield CCL nanoferrites were investigated by XRD, FTIR, STEM-EDX besides its sundry features; dielectric, magnetic, optical and photocatalytic activity using the identical instruments in previous works [13, 15].

3. Results And Discussion

3.1. Structural and morphologic investigations

3.1.1. XRD analysis

Figure 1 manifests the XRD diffractograms of $\text{Co}_{0.5}\text{Cu}_{0.5}\text{La}_x\text{Fe}_{2-x}\text{O}_4$ (CCL); ($0 \leq x \leq 0.15$) ferrite nanoparticles. The chart of pristine $\text{Co}_{0.5}\text{Cu}_{0.5}\text{Fe}_2\text{O}_4$ nanoferrite sample ($x = 0.0$) gives peaks at diffraction angles $2\theta = 18.3, 30.26, 35.65, 37.20, 43.30, 53.60, 57.20, 62.80$ and 74.24 that indexed to Miller notations as; 111, 220, 311, 222, 400, 422, 511, 440 and 533 in that order. Actually, these diffraction peaks are totally indexed to the FCC spinel lattice conforming to JCPDS cards (00-001-1121 and 01-077-0010). Also, the XRD of the reminder $\text{Co}_{0.5}\text{Cu}_{0.5}\text{La}_x\text{Fe}_{2-x}\text{O}_4$ ferrite nanoparticles have diffraction peaks congruous to those observed in the pristine sample with slightly shift for diffraction angles; which

confirm the spinel structure for all CCL nanoferrites. The substitution of La^{3+} not produces any impurities, or foreign phase; confirming the wholly dissolution of La^{3+} ions in CCL spinel lattice. Furthermore, the peaks are sharp and spread over the XRD patterns; affirming the nanocrystalline nature for all the investigated CCL nanoferrites.

The lattice parameter (a_{exp}) for all $\text{Co}_{0.5}\text{Cu}_{0.5}\text{La}_x\text{Fe}_{2-x}\text{O}_4$ nanoparticles is calculated using the related Eq. in [16]. Although the substitution process is a larger ion, La^{3+} (1.032 Å), instead of a smaller one, Fe^{3+} (0.645 Å) [17], the lattice parameter did not introduce an increment behavior. It has a peculiar trend; decrement from (8.375 Å at $x = 0.0$) - (8.327 Å at $x = 0.12$) and augment for the nanoferrite with $x = 0.15$ to 8.375 Å, see Fig. 2. Three hypotheses are further suggested to interpret this enigma; two for the decrement behavior and one for the increment situation. Firstly, microstrains are the reason for the a_{exp} decrement behavior, where make a compensation role against the large predictable crystal expansion. In fact, La^{3+} ions (with its large radius) tend to enlarge the a_{exp} values, then as a reparations for this alteration in spinel lattice, strain attempts to reduce it [18, 19]. Mariosi et al. [20], reported alike behavior for decreasing lattice parameter of $\text{CoLa}_x\text{Fe}_{2-x}\text{O}_4$ ferrite nanoparticles and explicated its behavior using the same reason. Secondly, bond dissociation energy (BDE) is another factor for interpreting this decrement behavior. In fact, BDE of (La–O) is (619 kJ/mol) which be larger than that of (Fe–O) (409 kJ/mol) [21]. Consequently, the La–O bond is shortened and sturdy; therefore, CCL lattice volume and consequently its parameter are decreased. As for the third hypothesis, it will be for the nanoferrite with $x = 0.15$; where its a_{exp} increment behavior can be interpreted in view of cations redistribution between tetrahedral (A) and octahedral (B) positions in CCL ferrite lattice. Actually, the ionic radii at A-sites are $r_A(\text{Co}^{2+}0.58 = (\text{Å})$, $r_A(\text{Cu}^{2+}0.57 = (\text{Å})$, $r_A(\text{Fe}^{3+}0.49 = (\text{Å})$, and at B-sites are $r_B(\text{Co}^{2+}0.745 = (\text{Å})$, $r_B(\text{Cu}^{2+}0.73 = (\text{Å})$, $r_B(\text{Fe}^{3+}0.645 = (\text{Å})$, $r_B(\text{La}^{3+}1.032 = (\text{Å})$ [17]. Then, the larger La cations will situate in B-site at expense of Fe^{3+} ones, which forced some Fe^{3+} cations to emigrate from B- to A-sites and consequently some Co^{2+} and Cu^{2+} , with their larger radii in B sites rather than in A-sites, will transfer from A- to B-sites; producing a_{exp} increment behavior for the nanoferrite with ($x = 0.15$). Ounacer et al. [22], declared a similar attitude and expound its result with the same reasoning.

Although, crystallite size can be determined by diverse methods; Rietvled, Williamson-Hall (W-H) or Scherrer's formula, W-H method is the most convenient one, because the strain components are involved. Consequently, the crystallite size ($D_{\text{W-H}}$) besides lattice strain (ϵ_s) of CCL ferrite nanoparticles is determined using Williamson-Hall method. Figure 3(a-f) shows the W-H graphs for all CCL nanoferrites, concerning the obtained diffraction peaks, with their better linear fitting; for determining crystallite size from intercept and lattice strain from the slope. Then crystallite size of CCL nanoferrites introduces distinctive trend; increment from 20.94 nm (at $x = 0.0$) to 33.01 nm (at $x = 0.09$) and then decrease step forward for $x = 0.12$ and 0.15 to 30.27 nm and 28.41 nm, respectively; see Fig. 2. This means that for small La^{3+} content, up to the nanoferrite with $x = 0.09$, the rates of nucleation and growth steps increase producing large size for crystallites [23]. Therefore, the high concentrations of La^{3+} ions ($x = 0.12$ and

Loading [MathJax]/jax/output/CommonHTML/jax.js grain boundaries pinning, and interns shackle grain growth;

resulting decreasing crystallite size trend for these two nanoferrite samples. On the other hand, lattice strains of CCL nanoferrites have positive values, see Fig. 2; demonstrating that all CCL nanoferrites possessing tensile strain with increasing values up to $x = 0.09$ and then decrease for further La^{3+} substitution. This increment behavior of lattice strain confirms the first hypothesis for lattice parameter decrement; as discussed above.

3.1.2. Morphological characterization

The STEM-EDX of some selective samples, $\text{Co}_{0.5}\text{Cu}_{0.5}\text{Fe}_2\text{O}_4$, $\text{Co}_{0.5}\text{Cu}_{0.5}\text{La}_{0.09}\text{Fe}_{1.91}\text{O}_4$ and $\text{Co}_{0.5}\text{Cu}_{0.5}\text{La}_{0.15}\text{Fe}_{1.85}\text{O}_4$ as manifested in Fig. 4(a-f). The STEM graphs, Fig. 4(a, c and e), demonstrate the nanocrystalline nature of all the samples. It is plainly noticed the STEM micrographs possess almost spherical crystallites which indiscriminately distributed throughout the ferrite sample surface. Furthermore, CCL samples show agglomeration partly, which emanates from its constituents magnetic nature in addition to binding forces among surface nanoparticles. To corroborate the existence of the different metals in CCL ferrite samples, EDX micrographs were utilized to this mission as seen in Fig. 4(b, d and f). Actually, the EDX charts of CCL powders affirmed existence of metal cations; La, Co, Fe, Cu and O ions with no others traces of impurity; asserting the purity of CCL nanoferrite samples even substituted by a rare earth element (La). Furthermore La/Fe atomic percent matches with the desired ratios; affirmed from La peaks leveraging on account of iron; as in Fig. 4(d,f). Additionally, atomic% ratio of $(\text{Co} + \text{Cu})/\text{Fe}$ and $(\text{Co} + \text{Cu})/(\text{Fe} + \text{La})$ is just about 0.5; corroborating, once more, the prepared powders purity. Furthermore, the characteristic mapping of $\text{Co}_{0.5}\text{Cu}_{0.5}\text{La}_{0.15}\text{Fe}_{1.85}\text{O}_4$ nanoferrite, for instance, Fig. 5, which reveals the constituent elements homogeneous distribution.

3.2. Magnetic properties

3.2.1. Magnetic parameters of CCL nanoferrites

The hysteresis loops for the $\text{Co}_{0.5}\text{Cu}_{0.5}\text{La}_x\text{Fe}_{2-x}\text{O}_4$ nanoferrites at room temperature ($\text{RT} = 303\text{K}$), utilizing a field to $\pm 20 \text{ kOe}$, are illustrated in Fig. 6. Then collected magnetic parameters; M_s , M_r and H_c of CCL nanoferrites are tabulated in Table 1. The M_s values are steadily diminishing with further substitution of La^{3+} ion; from $M_s = 53.67 \text{ emug}^{-1}$ (for $x = 0.0$) until $M_s = 42.75 \text{ emug}^{-1}$ (for $x = 0.15$). In fact, M_s values of ferrite materials are in straight proportionality with cations magnetic moment, which relies mainly on the unpaired (e) in the ferrite cations [24]. Hence, this progressively decrement in M_s values is a logical result to the magnetic moment difference for La/Fe cations, where La ($2.78 \mu_B$) and Fe ($5.92 \mu_B$); resulting deteriorating A-B super-exchange type [25]. Then remanent magnetizations of CCL nanoferrites introduce the identical trend as saturation magnetization, with the same dialectics, from 27.79 to 21.53 emug^{-1} ; with further La substitution.

Table 1

The lattice parameter (a_{exp}), crystallite size (D_{W-H}), saturation magnetization (M_s), remanent magnetization (M_r) and coercivity (H_C) initial permeability (μ_i), anisotropy constant (K) and microwave frequency (ω_M) of CCL nanoferrites.

x	a_{exp} (Å)	D_{W-H} (nm)	M_s (emu/g)	M_r (emu/g)	H_C (Oe)	μ_i	K (erg/cm ³)	ω_M (GHz)
0.0	8.375	20.94	53.67	27.79	1078.80	1.00	60311.66	11.87
0.03	8.375	21.56	51.53	25.95	1044.40	1.02	56060.35	11.40
0.06	8.330	25.58	51.07	26.03	957.73	1.31	50949.24	11.30
0.09	8.330	33.01	50.57	25.46	922.19	1.74	48578.28	11.19
0.12	8.327	30.27	43.86	22.03	1048.60	1.22	47907.91	9.70
0.15	8.375	28.41	42.75	21.53	1111.30	1.05	49487.58	9.46

Table 2

The kinetic rate constants (k_0 , k_1 and k_2) and correlation coefficient (R^2) for zeroth, first and second order reaction kinetics of RhB dye with and without CCL photocatalyst nanoparticles.

Sample	Kinetic model parameters		
	Zeroth order	First order	Second order
RhB	$k_0 = -1.23 \times 10^{-4}$	$k_1 = 1.76 \times 10^{-4}$	$k_2 = 2.52 \times 10^{-4}$
	$R^2 = 0.977$	$R^2 = 0.978$	$R^2 = 0.980$
RhB + Co _{0.5} Cu _{0.5} Fe ₂ O ₄	$k_0 = -9.11 \times 10^{-4}$	$k_1 = 0.00137$	$k_2 = 0.00207$
	$R^2 = 0.998$	$R^2 = 0.998$	$R^2 = 0.994$
RhB + Co _{0.5} Cu _{0.5} Sm _{0.09} Fe _{1.91} O ₄	$k_0 = -0.00459$	$k_1 = 0.01498$	$k_2 = 0.08797$
	$R^2 = 0.995$	$R^2 = 0.868$	$R^2 = 0.587$

For H_C values, it possesses a distinct trend; firstly presents a downward one, from 1078.8 to 922.19 Oe (for $0.0 \leq x \leq 0.09$), and an upward one from 922.19 to 1111.3 Oe (for $0.09 \leq x \leq 0.15$). This abnormal trend of H_C for CCL nanoferrites can be argued as follow. Firstly, the introduction of the nonmagnetic La³⁺ ions in CCL nanoferrites and its accompanied impact is diminishing saturation magnetization; therefore, the field needed to clobber this magnetization property to 0 levels, also, is decreased. Secondly the H_C behavior in the range $0.09 \leq x \leq 0.15$ has two reasoning. The first one is the CCL crystallite size impact; with its inversely proportional to coercivity [26]. As shown in Fig. 2, crystallite size of CCL nanoferrites in

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ent behavior. Hence, as the crystallite size diminishes as the

grain boundaries augment, i.e., the disordered regions increase and required coercivity field, H_C , as a result increase. The second one is magneto-crystalline anisotropy of the substituted rare earth element (La) which increases the coercivity of the resultant ferrite. Actually, in materials containing heavy rare-earth elements, the spin–orbit coupling is strong. Once magnetized, a high field must be utilized to reverse the magnetization direction after conquer the anisotropy produced from this coupling [27]. Thus, with further La substitution, in the span $0.09 \leq x \leq 0.15$, spin-orbit coupling and consequently the magneto-crystalline anisotropy of CCL nanoferrites increase and hence H_C value increases. At last, it is concluded that the CCL samples have hard magnetic features which can be adjusted by La^{3+} ions substitutions. Finally, the nanoferrite $\text{Co}_{0.5}\text{Cu}_{0.5}\text{La}_{0.15}\text{Fe}_{1.85}\text{O}_4$ have a moderate saturation value 42.75 emu/g and the highest coercivity value 1111.3 Oe; candidate it to be an effective material for storage and recording applications.

Additionally, initial permeability and anisotropy constant of the $\text{Co}_{0.5}\text{Cu}_{0.5}\text{La}_x\text{Fe}_{2-x}\text{O}_4$ nanoferrites are calculated using the Ref. [28, 29], and tabulated in Table 1.

$$\text{Anisotropy constant}(K) = \frac{M_S \times H_C}{0.96}$$

$$\text{Initial permeability}(\mu_i) = \frac{M_S^2 \times D_{W-H}}{K}$$

In fact, initial permeability has a distinctive attitude with La/Fe substitution process; increasing behavior for the nanoferrites with $0.00 \leq x \leq 0.09$ and a decreasing one for $x = 0.12$ and 0.15 nanoferrites. Although, saturation magnetization has a regular decrement behavior, μ_i introduces this abnormal demeanor. Indeed the impact of crystallite size and anisotropy constant are decision makers for μ_i behavior. Thus La substitution in Co-Cu nanoferrites, in the range $0.00 \leq x \leq 0.09$, supports magnetic flux to pass and concentrate within these nanoferrites and inhibit it for $x = 0.12$ and 0.15 nanoferrites. Contrary to expected results anisotropy constant introduces a decrement behavior with La/Fe substitution process. Where, it was expected that the spin-orbital coupling of La ions can enhance anisotropy property of these nanoferrites.

3.2.2. High frequency response of CCL ferrite nanoparticles

Basically, ferrite materials are the only ones available for microwave realm applications. Where for frequency ($1 \text{ GHz} \leq f \leq 1000 \text{ GHz}$), the electrical energy is not transported via wires, but through electromagnetic waves which contained in wave-guides and transmitted through space. So we have to investigate the high frequency response of the prepared CCL nanoferrites to discover their applications in microwave fields. The microwave frequency (ω_M) values for all CCL nanoparticles are determined using Ref. [30] and then saved in Table 1. From the calculated ω_M values, 11.87 GHz–9.46 GHz, CCL nanoferrites may be employing in high frequency applications. These values introduce a significant progress compared with other systems containing different rare earth elements with maximum ω_M value 8.4 GHz [31]

3.2.3. Switching field distributions (SFD) response of CCL ferrite nanoparticles

Figure 7, with its inset curve, shows the SFD plots (dM/dH vs. H) of all CCL nanoferrites. Physically, SFD plots scout the constituting cations exchange coupling. All SFD curves acquire higher values at large reverse field meanwhile introduce an almost constant one for higher fields; affirming the vigorous cations exchanges at higher reverse field. Then inset plot, for large reverse field; confirming those figures are discontinuous. Analogous behavior was declared regarding different ferrites containing diverse rare earth elements [31].

3.3. Dielectric properties

Regarding to dielectric bounds of La- substituted Co-Cu ferrite nanoparticles, special studies have been investigated. Actually, in frequency span (50Hz-5MHz at RT), dielectric parameters (dielectric constant, ϵ' , and loss tangent, $\tan\delta$) besides conductivity (σ_{ac}) for the synthesized system of $Co_{0.5}Cu_{0.5}La_xFe_{2-x}O_4$ nanoparticles have been studied. Fundamentally, ϵ' refers to the amount of stored energy in the ferrite material, whereas $\tan\delta$ gives the energy loss out of phase rather than the response of the material, whilst σ_{ac} determines the kind and mechanization of conduction within an applied field. Actually, the ϵ' and σ_{ac} results of $Co_{0.5}Cu_{0.5}La_xFe_{2-x}O_4$ samples are determined using the Ref. [32], whilst $\tan\delta$ result is getting directly from the instrument. As noticed in Fig. 8(a) ϵ' decreases more speedily in the frequency then becomes dormant as frequency augment; which is the typical demeanor of all ferrite [33]. Based on Koop's model, any ferrite structure formed by arrangement of conducting regions (grains) estranged with lower conducting regions (grain boundaries) [34]. Hence at lower frEq. region various charge carriers transfer among dissimilar ions of the same element, e.g., Fe^{2+} & Fe^{3+} , which accumulate on grain boundaries (GBs); due to it high resistivity. This phenomenon is called Maxwell-Wagner (M-W) polarization which gives a high value of dielectric constant which decreases slowly with frequency [35]. At higher frEq. these charges within grains itself cannot pursue the frequency of the applicable field, and then polarization diminishing and almost stable ϵ' level is obtained [36]. As observed from inset curve of Fig. 8(a), the dielectric constant of CCL nanoferrites decrease gradually with further La^{3+} substitution in view of two respects. The first one is the electron hopping among Fe^{2+} & Fe^{3+} ions reduces by La^{3+}/Fe^{3+} ions replacement. The second is account for the increment of resistivity, originated from 3d-4f coupling of La ions, where the relation between resistivity and ϵ' is inversely proportion [37].

As for the σ_{ac} behavior, it has a growing attitude with frequency; see Fig. 8(b). Many workers declared that presence similarity for σ_{ac} and ϵ' mechanisms for ferrite materials [38–40]. Consequently, the preceding interpretation of ϵ' for CCL nanoferrites is benefit for understanding σ_{ac} behavior with frequency. Hence, as noticed from the inset curve of Fig. 8(b), σ_{ac} decreases with the augment in La content. As for conductivity frequency dependence, the crowd of charges on CCL nanoferrites GBs is the major cause for the independent regime in σ_{ac} plot. By increasing frequency, the impact of interior Gs of CCL nanoferrites and charge carriers transfer are accountable for σ_{ac} increment demeanor. Generally, frequency acts to

augment the conduction phenomenon by its propelling diverse charge carriers between the conduction positions [41].

The $\tan\delta$ of the investigated CCL ferrite nanoparticles is given in Fig. 8(c). In fact, the decreases in $\tan\delta$ value are noticed with further increasing frequency and with La^{3+} ions substitution; see the inset curve of Fig. 8(c). This behavior of $\tan\delta$ can be justified using two facts. With increasing La content in CCL nanoferrites, polarization (ϵ'') depressed and also the accompanied loss decrease; this is the first reason. The other cause for $\tan\delta$ behavior is the CCL crystallite size by it's inversely proportion with it [42].

3.4. Optical studies

3.4.1. UV-Visible absorption and optical energy gap

For the present $\text{Co}_{0.5}\text{Cu}_{0.5}\text{La}_x\text{Fe}_{2-x}\text{O}_4$; ($x = 0.0, 0.03, 0.06, 0.09, 0.12, 0.15$) ferrite nanoparticles, one can notice a broad absorption band positioned nearly at 500 nm; as shown in Fig. 9. Generally, ferrite materials are opaque at wavelengths ≤ 200 nm; at which the photon energy is $\geq$ optical band gap (E_g), which is required for transition from valence to conduction bands [43]. The E_g values of $\text{Co}_{0.5}\text{Cu}_{0.5}\text{La}_x\text{Fe}_{2-x}\text{O}_4$ nanoferrites can be calculated by extrapolating the linear portion curve of $(\alpha h\nu)^2$ vs. photon energy ($h\nu$) to $(\alpha h\nu)^2 = 0$; for direct allowed transition (Tauc's plot) (Fig. 10(a-f)) [44]. From Tauc's plot, E_g values of CCL nanoferrites are determined. Basically, the band gap can be tuned based on several factors: e.g., crystallite size, structural parameter and impurities. The calculated E_g values of CCL nanoferrites are displayed in Fig. 11. In fact our energy gap possesses a peculiar demeanor; a red shift from 3.04 eV to 2.46 eV (for $0.0 \leq x \leq 0.09$) and a blue shift from 2.46 eV to 2.98 eV for ($0.09 \leq x \leq 0.15$). A similar E_g behavior was observed in an earlier work for Zn-Mg nanoferrites [13]. This behavior of E_g can be explained through two scenarios. Firstly, further La content generates a lot of donor levels in the forbidden band, producing E_g decrement. Secondly, this tendency of E_g may be accredited to the decrement attitude of CCL nanoferrites crystallite size in the range $0.09 \leq x \leq 0.15$ (see Fig. 2); where the relationship between the band gap and particle size is an inversely one [15]. Also the augmentation of conductivity of Co-Cu nanoferrites with further La^{3+} substituting confirms the E_g behavior in that range.

3.4.2. Photocatalytic activity

The influence of $\text{Co}_{0.5}\text{Cu}_{0.5}\text{La}_x\text{Fe}_{2-x}\text{O}_4$ nanoferrites on photo-catalytic dye degradation of Rhodamine B (RhB) was investigated using absorption spectra. However, the E_g of photocatalyst governs the absorbed wavelength and produces electron-hole pairs. The nanoferrite specimens with $x = 0.0$ and 0.09 La^{3+} were chosen for this investigation because $x = 0.0$ represent the pristine ferrite and $x = 0.09$ has the least E_g value. This choice based on the opposite relation between E_g and photodegradation behavior [13]. Moreover, the replacement of rare earth cations in Co-Cu ferrite gives good optical absorption in visible range point toward enhanced photodegradation efficiency. As a consequence of metastable La-4f energy levels creation near the lower edge of the conduction band of Co-Cu ferrite, this indicates the decrease in

the band gap. A further factor is the defects resulting from La doping which act as trapping centers and simplify the split-up of photogenerated electron-hole pairs and increase the life time of charge carrier [45].

The photo-catalytic degradation efficiency is obtained from the variation in Absorbance for the reason of direct relation between concentration (c) and absorbance (A) [46]. It is well known that, the self-degradation efficiency of RhB (without catalyst) is very small value for dye disposal [13]. Figure 12(a-c) manifests photocatalytic degradation of RhB and RhB + $\text{Co}_{0.5}\text{Cu}_{0.5}\text{La}_x\text{Fe}_{2-x}\text{O}_4$ ($x = 0.0$, and 0.09) irradiated under solar light at variable times (from 0-180 min). The reduction in absorbance intensity designates enhancement in dye degradation. The mechanism for RhB photodegradation of the nanoferrite in which $x = 0.9$ La (as an example) is understood with aid of some of free radicals. All the spectra evident the characteristic absorption curves of RhB with a peak, at ~ 552 nm and a shoulder at ~ 512 nm [47].

The % degradation of samples is determined via the equation listed in Ref. [48]. Figure 13 illustrates % degradation for pure RhB and RhB over CCL nanoferrites with ($x = 0.0$ and 0.09). The % degradation, after irradiation for 180 min, of pure RhB dye is just 3.31%; which is an unsatisfactory impact. As for the % degradation for RhB over CCL nanoferrites with ($x = 0.0$ and 0.09) photocatalysts is enlarged; (22.37% and 94.50%, respectively). Hence, the catalytic recital was enhanced with La/Fe substitution process via the next most probable discussion. When the electrons were excited from valence band (VB) to created energy level CCL conduction band (CB) in the sample under sunlight irradiation, the photogenerated holes in VB react with surface water or hydroxyl ion to yield $\text{OH}^\bullet$ radical, which is a good oxidant in the degradation of RhB and instantaneously, electrons in the CB reacts with adsorbed oxygen molecule to yield $\text{O}_2^{\bullet-}$. Moreover, it combines with H^+ to yield HO_2 . [49], which react with trapped electrons to yield $\text{OH}^\bullet$ [50]. It is obvious that, $\text{OH}^\bullet$, HO_2 , $\text{O}_2^{\bullet-}$ and h_{VB}^+ are active species included in RhB photodegradation. Regarding the previous argument, the photochemical reaction for the degradation of RhB under sunlight irradiation of Co-Cu-La ferrite photocatalyst was summarized as follows [13].

These radicals, formed from the previous steps, can interact with the toxic RhB dyes, converting its complex molecules to simple and non-toxic ones. Dhiman et al. [51] in previous work obtain comparable mechanisms for photocatalytic behaviors for CoFe_2O_4 ferrite doped with various rare earths.

To distinguish the photocatalytic activity protocol of CCL photocatalyst, the three kinetic models (0th, 1st and 2nd orders) are determined using the following equations [52].

$$A_t = A_o - k_0 t, A_t = A_o e^{-k_1 t}, \frac{1}{A_t} = \frac{1}{A_o} + k_2 t$$

where A_t and A_o are absorbance of RhB dye after and before irradiation time (t), respectively. For this mission, the plots of A_t , $\ln(A_o/A)$ and $1/A_t$ versus time are determined with their linear fitting; see Fig. 14(a-c). The three kinetic constants (k_0 , k_1 and k_2) of zeroth, first and second order reaction kinetics, respectively of RhB and (RhB + CCL samples ($x = 0.0$ and 0.09)) are calculated and tabulated in Table 2. Also, correlation coefficient (R^2) of each order kinetic is calculated and inserted in Table 2. The second order is the most favorable model for pure RhB, where its R^2 value is 0.980 (the highest value compared with other orders). As for RhB over CCL sample with ($x = 0.0$) has R^2 value 0.998 for both zeroth and first-orders; declaring that these models are favorable models for degradation. Meanwhile for RhB over CCL sample with ($x = 0.09$) has R^2 value 0.995 for zeroth; demonstrating this model is the most suitable model for degradation of this sample. Finally, the k_0 , k_1 and k_2 values for RhB dye degradations in presence of CCL nanoferrite powders are higher than those of pristine RhB dye; see Table 2. These outcomes confirm the CCL nanoferrites are capable of enhancing the RhB dye degradation efficiency in industrial community.

Conclusion

A sequence of lanthanum substituted cobalt-copper ($\text{Co}_{0.5}\text{Cu}_{0.5}\text{La}_x\text{Fe}_{2-x}\text{O}_4$; $0 \leq x \leq 0.15$) (CCL) were prepared via a combustion approach. XRD charts of CCL samples affirmed the spinel structure for the prepared powders. Although the substitution process is a larger ion, La^{3+} (1.032 Å), instead of a smaller one, Fe^{3+} (0.645 Å), the lattice parameter did not introduce an increment behavior. It has a peculiar trend; decrement from (8.375 Å at $x = 0.0$) to (8.327 Å at $x = 0.12$) then augment for the nanoferrite with $x = 0.15$ to 8.375 Å. The crystallite size of CCL nanoferrites introduces a distinctive trend; increment from (20.94 nm at $x = 0.0$) to (33.01 nm at $x = 0.09$) then decrease step forward for $x = 0.12$ and 0.15 to 30.27 nm and 28.41 nm, respectively. STEM micrographs possess almost spherical crystallites which indiscriminately distributed throughout the ferrite sample surface. M_s values are steadily diminishing with further substitution of La^{3+} ion; from $M_s = 53.67 \text{ emug}^{-1}$ (for $x = 0.0$) to $M_s = 42.75 \text{ emug}^{-1}$ at ($x = 0.15$). H_c values, it possesses a distinct trend; firstly presents a downward one, from 1078.8 to 922.19 Oe (for $0.0 \leq x \leq 0.09$), and an upward one from 922.19 to 1111.3 Oe (for $0.09 \leq x \leq 0.15$). Dielectric constant and loss tangent have a decrement behavior with frequency and with substitution of La ions. E_g has a peculiar demeanor; a red shift from 3.04 eV to 2.46 eV (for $0.0 \leq x \leq 0.09$) and a blue shift from 2.46 eV to 2.98 eV for ($0.09 \leq x \leq 0.15$). The % degradation for RhB over CCL nanoferrites with ($x = 0.0$ and 0.09) photocatalysts is enlarged; (22.37% and 94.50%, respectively). The nanoferrite $\text{Co}_{0.5}\text{Cu}_{0.5}\text{La}_{0.15}\text{Fe}_{1.85}\text{O}_4$ has a moderate saturation magnetization, highest coercivity and lowest loss which can be a suitable candidate for data

storage applications. Moreover, $\text{Co}_{0.5}\text{Cu}_{0.5}\text{La}_{0.15}\text{Fe}_{1.85}\text{O}_4$ can be utilized as a photocatalyst for RhB effluents removal with degradation efficiency 94.50% at 180 min.

Declarations

Acknowledgements

“This research work was funded by Institutional Fund Projects under grant no. (IFPHI-165-247-2020). Therefore, authors gratefully acknowledge technical and financial support from the Ministry of Education and King Abdulaziz University, DSR, Jeddah, Saudi Arabia”.

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Figures

Figure 1

XRD diffractograms of $\text{Co}_{0.5}\text{Cu}_{0.5}\text{La}_x\text{Fe}_{2-x}\text{O}_4$; ($0.0 \leq x \leq 0.15$) nanoferrires.

Figure 2

Dependence of lattice constant (aexp), crystallite size (WD-H) and lattice strain of on La3+ content for CCL nanoferrites.

Figure 3

(g) WD-H plot of $\text{Co}_{0.50}\text{Fe}_{0.50}\text{La}_x\text{Fe}_{2-x}\text{O}_4$ ($0.00 \leq x \leq 0.15$) nanoferrites.

Figure 4

(a-f): FE-SEM-EDX micrographs of (a) $\text{Co}_{0.5}\text{Cu}_{0.5}\text{Fe}_2\text{O}_4$, (b) $\text{Co}_{0.5}\text{Cu}_{0.5}\text{La}_{0.09}\text{Fe}_{1.91}\text{O}_4$ and (c) $\text{Co}_{0.5}\text{Cu}_{0.5}\text{La}_{0.15}\text{Fe}_{1.85}\text{O}_4$ ferrite nanoparticles.

Figure 5

Typical STEM-EDX mapping for $\text{Co}_{0.5}\text{Cu}_{0.5}\text{La}_{0.15}\text{Fe}_{1.85}\text{O}_4$ ferrite nanoparticles.

Figure 6

Hysteresis loops of CCL nanoferrites at RT.

Figure 7

SFD response of CCL nanoferrites with its inset curve.

Figure 8

(a-c): The frequency dependence of (a) ϵ' , (b) σ_{ac} and (c) $\tan\delta$ for CCL nanoferrites at RT.

Figure 9

Optical absorption spectra as a function of wavelength for the prepared nanoferrite samples.

Figure 10

(a-f): Tauc's plot for all CCL nanoferrites.

Figure 11

The change of E_g versus La^{3+} content.

Figure 12

(a–c): Absorbance spectra of (a): pure RhB, (b): RhB with the $\text{Co}_{0.5}\text{Cu}_{0.5}\text{Fe}_2\text{O}_4$ nanoferrite and c): RhB with the $\text{Co}_{0.5}\text{Cu}_{0.5}\text{La}_{0.09}\text{Fe}_{1.91}\text{O}_4$ nanoferrite; taken at different photocatalytic degradation times (0–180min).

Figure 13

% degradation plot of pure RhB and RhB over Co_{0.5}Cu_{0.5}S_mxFe_{2-x}O₄; (0.0 and 0.09) nanoferrites, under simulated sunlight irradiation up to 180 min.

Figure 14

(a-c): The plots of (a) A_t , (b) $\ln(A_o/A_t)$ and (c) $(1/A_t)$ for RhB dye without and with $\text{Co}_{0.5}\text{Cu}_{0.5}\text{La}_x\text{Fe}_{2-x}\text{O}_4$; ($x=0.0$ and 0.09) as photocatalysts.