Influence of rare earth ion substitutions on the structural, optical, transport, dielectric, and magnetic properties of superparamagnetic iron oxide nanoparticles

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Abstract: Superparamagnetic Fe₃O₄ and RE:Fe₃O₄ (RE = Dy, Nd, La) nanoparticles with an average crystallite size in the range of 15–24 nm, were synthesized by co-precipitation method. The samples were characterized using X-ray diffraction (XRD), scanning electron microscopy (SEM), vibrating sample magnetometer (VSM), UV–Vis spectroscopy, LCR bridge, and two-probe technique. X-ray diffraction patterns of all the investigated samples reveal the typical phase of magnetite structure, with a small contribution of orthoferrite (NdFeO₃) as a secondary phase in Nd:Fe₃O₄ sample. The saturation magnetization (M_s) of the samples has values in the range from 41.8 to 52.3 emu/g, and decreases with RE ion doping depending on the ionic radius. Negligible values of the coercivity H_c and remanence M_r , indicate the superparamagnetic nature of the investigated samples. The calculated values of indirect optical band gap of Fe₃O₄ and RE:Fe₃O₄ nanoparticles are in the range of 0.9–1.25 eV. The dielectric constant of the samples decreases, while their activation energy increases with the increasing of ionic radii of dopants.

Keywords: superparamagnetic iron oxide nanoparticles (SPIONs); rare earth (RE) ions; structure, optical and activation energies; electrical conductivity; dielectric constant; saturation magnetization

1 Introduction

Nanoparticles (NPs) have received a lot of attention in the last decade due to their unique properties and potential to be used in a wide range of applications [1]. Among all types of nanoparticles, biocompatible iron oxide nanoparticles (IONs) are used for various

biomedical applications [2]. At present, IONs have been found very suitable and highly applicable in lithium ion batteries [3], catalysis [4], as well as supercapacitors [5]. The magnetic behavior of IONs greatly depends on their size, shape, purity, and crystal structure, which determine their applications. For instance, the size of magnetic particles typically used in biomedicine needs to be in the nanoscale range [6], so that their dimensions are smaller than or comparable to those of cell, virus, protein, or gene [7]. However,

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the smallest sized nanoparticles are not necessarily the best because they are often associated with very small magnetic moments which dramatically increase difficulties in manipulating the particles for applications with an external magnetic field at ambient temperature [8]. When the size decreases to a critical value (20–30 nm), the magnetite nanoparticles become superparamagnetic at room temperature, as their magnetic moments are thermally equilibrated [8–13]. Due to their small size and surface area characteristics, they exhibit unique electronic, optical, and magnetic properties that can be exploited for drug delivery [14,15]. Superparamagnetic iron oxide nanoparticles (SPIONs) are especially interesting in thermal therapy, tumor and cancer diagnosis and treatment [7], and diagnostic magnetic resonance imaging [16]. Transition metals (Co, Ni, Mn, and Pt) are known to be effective dopants of magnetic nanoparticles (MNPs) with the scope to improve their magnetic properties [17]. Recently, MNPs engineered by RE ion doping have attracted considerable attention due to their wide applications in biology, catalysis, and solar cells [13, 18,19]. Compared to the transition metal, RE has much stronger potential in expressing pronounced magnetic features due to large unquenched orbital angular momentum attributed to the f electrons demonstrating higher spin–orbit coupling [20–23]. Since crystal-field effects are smaller and spin–orbit coupling is larger for f electrons compared to the d electrons of transition metal ions, the orbital component of the magnetic moment is much more important for the RE ions compared to the transition metal ions. Also the unique f-electronic structure of metals in the rare earth series allows materials made from these elements to potentially exhibit very useful magnetic properties. This is why the substitution of Fe^{3+} in magnetite with rare earth ions could improve the magnetic, electrical, and optical properties of IONs and reduce the oxidation of them [20,21,23]. When Fe_3O_4 is doped with RE ions, their 4f occupancy, number of unpaired 4f electrons, and their ionic radii play a crucial role in determining various functional properties of the material [24,25]. It is known that the magnetic behavior of the ferrimagnetic oxide compounds is largely governed by the Fe–Fe interaction (the coupling of the spin of the 3d electrons). By introducing rare earth ions (RE^{3+}) in spinel lattice, RE^{3+} – Fe^{3+} interactions appear, which can lead to changes in the magnetization [26]. The effects of rare earth (RE) element (La, Nd, Gd) doping on the

structure and magnetic properties of MnZn ferrite nanoparticles were investigated [27]. It was found that the particle size, saturation magnetization (M_s), and coercive force (H_c) strongly depend on the RE concentration due to the preferred occupied positions of RE ions [27]. The VSM data indicated that an improvement in the superparamagnetic behavior of IONs is obtained as a result of La^{3+} doped IONs, where La-IONs exhibited smaller remanent magnetization (M_r) and coercivity (H_c) values as compared with undoped IONs [28]. The estimated saturation magnetization of $\text{Eu:Fe}_3\text{O}_4$ NPs (7.0 emu/g) is smaller than that of $\text{Gd:Fe}_3\text{O}_4$ NPs (15 emu/g) at 300 K [13]. Douglas *et al.* [1] prepared IONs doped with Gd^{3+} ions by a surfactant-assisted thermolysis route. They measured the saturation magnetization (32.9 and 28.9 emu/g at 100 and 300 K respectively) and the specific absorption rate ($3.7 \pm 0.6 \text{ W/g}_{\text{Fe}}$ when $H_0 = 3 \text{ kA/m}$ and $f = 111 \text{ kHz}$). Authors suggested that Gd doped ION particles are viable candidates for magnetic hyperthermia (MH) applications [1] and an effective route for the fabrication of dual modal MRI contrast agents [1,12,29,30]. There are earlier reports on the magnetic properties of different rare earth ions (RE = Dy, Gd, Sm, Eu, Ho) [1,31–34].

To the best of our knowledge, the optical, electrical, dielectric, and magnetic properties of RE^{3+} (Dy^{3+} , Nd^{3+} , La^{3+}) doped SPIONs have not been reported until now. Therefore, effect of the three different rare earth dopants on the properties of SPIONs is reported here.

2 Experimental techniques

2.1 Materials

Ferric nitrites nonhydrate $\text{Fe}(\text{NO}_3)_3$, lanthanum nitrites $\text{La}(\text{NO}_3)_3$, neodymium nitrites $\text{Nd}(\text{NO}_3)_3$, dysprosium nitrites $\text{Dy}(\text{NO}_3)_3$, ferrous sulfate FeSO_4 , and ammonia solution (25%) were purchased from Sigma.

2.2 Synthesis of superparamagnetic iron oxide nanoparticles (SPIONs)

SPIONs were prepared by co-precipitation technique. Ferric nitrites and ferrous sulfate were mixed in 2:1 molar ratio. The solutions of ferrous and ferric were prepared by adding their salts to distilled water and mixing them very well with magnetic stirrer for 30 min. Then, the solution was precipitated by ammonia

solution at pH = 11 (the optimum pH value [35]) with continuous stirring by rate 7500 rpm at 50 °C. Brown colored particles of iron oxide were precipitated. After that, the particles were separated from the solution by using a strong magnet and they were washed many times with distilled water and ethanol until pH came down to 7. The powder was then dried in hot air oven at 90 °C for 48 h.

2.3 Synthesis of superparamagnetic iron oxide nanoparticles doped with rare earth ions (RE:SPIONs)

RE:SPIONs (RE = Dy, Nd, La) were prepared by co-precipitation technique. Ferric, ferrous, and rare earth (Dy, Nd, La) salts were mixed in 1.95:1:0.05 molar ratio and dissolved in deionized water. Then, the solutions tracked the same steps in the previous section.

2.4 Characterizations of SPIONs and RE:SPIONs

The microstructure of the investigated samples was characterized by powder X-ray diffractometer (Shimadzu LabX XRD-6000) of monochromatic Cu K α (λ = 1.54051 Å) radiation source operated at voltage 40 kV and current 25 mA with constant scanning speed of 2 (°)/min in the angular range of 2θ from 10° to 70°. The morphology of the investigated samples was examined by using a JEOL JSM-6360LV scanning electron microscope (SEM). The magnetic properties of the samples carried out by vibrating sample magnetometers (VSM Lakeshore model 7410) at room temperature with maximum applied field of 20 kOe. JASCO V-570 spectrophotometer was used to measure the absorbance, $\text{abs}(\lambda)$, of the samples over the wavelength range of 200–800 nm to estimate the variation of optical absorption and optical band gap of SPIONs and RE:SPIONs. The powder nanoparticle samples were pressed uniaxially using a hydraulic press into about a 2 mm thick disc with a diameter of 14 mm for 3 min, and then silver paint was applied on the flat surfaces of the discs and air-dried to have good ohmic contacts. Using disc samples, the dielectric behavior and AC conductivity were carried out by LCR bridge meter (Agilent 4284A Precision LCR Meter) as a function of frequency (1 kHz–1 MHz) at room temperature. The DC conductivity of the samples was measured as a function of temperature ranging from room temperature to 380 K by using two-probe experimental set-ups (Model DNM-121, SES Instruments Pvt. Ltd, Roorkee, India).

3 Results and discussion

3.1 Structural properties

Figure 1 shows the XRD patterns of SPIONs and RE:SPIONs. The observed diffraction peaks of Fe₃O₄, Dy:Fe₃O₄, and La:Fe₃O₄ samples indicate that these samples have the crystal phase of Fe₃O₄ (reference code 85-1436). This result confirms that, substitution of Fe³⁺ ions with Dy³⁺ and La³⁺ ones occurs inside the spinel crystal structure [27]. As shown in Fig. 1, the X-ray diffraction pattern of Nd:Fe₃O₄ reveals a single phase of Fe₃O₄ structure with minor peak corresponding to orthoferrite NdFeO₃ phase [35] (reference code 01-082-2421). The formation of NdFeO₃ phase may be attributed to the Nd³⁺ content exceeding a percolation threshold for incorporation into the spinel lattice. At this point, instead of occupying the Fe³⁺ sites in the lattice, Nd³⁺ forms the secondary phase which prefers to be localized on the surface of Nd:Fe₃O₄ nanoparticles. The amount of rare earth ions incorporated into Fe₃O₄ lattice could be determined by the ionic radii of rare earth ions [36]. The ionic radii of Dy³⁺, Nd³⁺, and La³⁺ are 0.94 Å, 1.08 Å, and 1.15 Å, respectively [37–39]. Therefore, the smallest ions of Dy³⁺ are incorporated into the inverse spinel lattice of Fe₃O₄ more readily than Nd³⁺ and La³⁺. The secondary phase is absent in La:Fe₃O₄ sample even though La³⁺ ions have a largest radius (r = 1.15 Å) [5]. It may be due to the paramagnetic character of La³⁺ ions [40].

Fig. 1 X-ray diffraction patterns of SPIONs and RE:SPIONs samples.

The structural parameters (the average lattice constant a , the average crystallite size D , and the average strain S) of all the SPIONs and RE:SPIONs samples were calculated by using X'pert high score plus software and plotted in Fig. 2. From Fig. 2(a), it can be seen that the lattice constant of RE:Fe₃O₄ nanoparticles is smaller than that of pure Fe₃O₄ nanoparticles, and this result agrees with results of many previous studies [27]. It is found that lattice constant a decreases with ionic radii of RE dopants. The decrease in lattice constant of IONs by the rare earth ion dopants is due to the occupancy of rare earth ions in B-sites [22,41] and the iron vacancies in these samples, as described in previous study [42]. Besides that, the Nd:Fe₃O₄ sample doped with Nd³⁺ ions has the smallest value of lattice constant, which may be attributed to extra stress and further compression of lattice induced by the secondary phase on the surface. All surface atoms of the lattice experience net cohesive force towards the center, and as a result lattice starts to shrink and lattice constant is reduced [43]. The crystallite size of the particles was estimated using X'pert high score plus software according to Debye–Scherrer formula. It was found to be in the nanometer range between 15 and 24 nm. Figure 2(b) shows that the crystallite size of the RE:Fe₃O₄ samples is greater than that of the Fe₃O₄ sample. The increase in crystallite size can be explained by the substitution of large ionic radii of Dy³⁺ (0.94 Å), Nd³⁺ (1.08 Å), and La³⁺ (1.15 Å) instead of small ionic radius of Fe³⁺ (0.64 Å) ions [37–39]. The average crystallite size value of Nd:Fe₃O₄ sample is smaller than that of Dy:Fe₃O₄, which can be attributed to two reasons: the first is that while a small amount of Nd³⁺ ions were entered to Fe₃O₄ lattice, all Dy³⁺ ions were entered completely to it. The second one retains to the secondary (orthoferrite) phase NdFeO₃ on the surface of Nd:Fe₃O₄ nanoparticles, which forms extra strain, as can be seen in Fig. 2(c) and therefore leads to shrinking of them. From Fig. 1, it can be observed that the strongest diffraction peak corresponding to (311) plane of Fe₃O₄ shifts slightly to higher 2θ value with respect to RE:Fe₃O₄ samples, which means that the lattice strain is reduced by the dopant ions as can be noticed in Fig. 2(c). The oxygen framework in Fe₃O₄ is fairly open and flexible and it can expand or contract without much strain to accommodate ions of larger size than interstitial sites [44].

Fig. 2 (a) Lattice constant, (b) crystallite size, and (c) strain of the SPIONs and RE:SPIONs samples.

Figure 3 shows the SEM images of the SPIONs and RE:SPIONs. The SEM micrograph confirms nano-size of the particles. In addition, the particles are uniformly aggregated, spherical shaped. The nanoparticles are agglomerated due to high dipole–dipole interactions among the uncapped nanoparticles, and to magnetostatic interaction. The effect of RE dopants on size of the Fe₃O₄ particles is not clear and its estimation from the SEM images is difficult.

Fig. 3 SEM images of the SPIONs and RE:SPIONs samples.

3.2 Optical properties

Figure 4 shows the absorption spectra of the SPIONs and RE:SPIONs at room temperature. The wavelength of the absorption peak of all the samples has been determined from the absorption spectrum curve in Fig. 4 and listed in Table 1. From Table 1, it can be seen that the absorbance peak wavelength (374 nm) of pure Fe_3O_4 nanoparticles is higher than the absorbance peak wavelengths of RE: Fe_3O_4 samples. The whole absorbance peaks of the investigated samples can be shown in the range from 342 to 374 nm, and this result agrees well with the literature [45]. This means the absorbance peaks in the UV and near visible ranges of electromagnetic spectrum and molecules of the samples undergo electronic transitions. These peaks are observed due to charge transfer between the Fe^{2+} and Fe^{3+} cations present in the octahedral and tetrahedral sites of the investigated samples.

Both the energy band gaps were calculated using the Tauc equation, $\alpha h\nu = B(h\nu - E_g)^n$, where $h\nu$ is the incident photon energy, α is the absorption coefficient, B is a material-dependent constant, and E_g is the optical band gap [46]. The value of n depends on the nature of transition. For direct allowed transition, $n =$

Fig. 4 Absorption spectra of the SPIONs and RE:SPIONs samples at room temperature.

Table 1 Absorbance peak wavelengths and direct and indirect optical gaps of the SPIONs and RE:SPIONs samples

Sample	Abs. peak (nm)	Direct E_g (eV)	Indirect E_g (eV)
Fe_3O_4	374	2.25	0.9
$\text{Dy:Fe}_3\text{O}_4$	342	3.2	1.1
$\text{Nd:Fe}_3\text{O}_4$	346	3.5	1.2
$\text{La:Fe}_3\text{O}_4$	344	3.55	1.25

1/2, and for indirect allowed transition, $n = 2$. Tauc plots drawn for indirect and direct transitions are shown in Fig. 5 and Fig. 6, respectively.

The energy band gap values of the investigated samples were calculated by extrapolating the linear portion of the curve represented to $\alpha h\nu = 0$. The investigated samples show both direct and indirect band gaps, which agree with previous report [47]. The calculated values of the direct and indirect band gap values are listed in Table 1. The direct band gap values are found to be greater than the indirect band gap for the all samples. Both the direct and indirect band gap values for the RE: Fe_3O_4 nanoparticles are found to be greater than that of the Fe_3O_4 . This result can be interpreted on the basis of the electronic transition of Fe^{3+} (level d)– O^{2-} (level p)– Fe^{2+} (level d) in pure Fe_3O_4 , in addition to the electronic transition of RE^{3+} (level f)–

Fig. 5 $(\alpha h\nu)^{1/2}$ versus photon energy ($h\nu$) of the SPIONs and RE:SPIONs samples.

Fig. 6 $(\alpha h\nu)^2$ versus photon energy ($h\nu$) for of the SPIONs and RE:SPIONs samples.

O^{2-} (level p)– Fe^{2+} (level d) in RE: Fe_3O_4 samples. The calculated values of direct and indirect optical band gap of pure Fe_3O_4 samples are equal to 2.25 and 0.9 eV respectively. The values of both direct and indirect energy band gaps are in the range of semiconductor energy band gap 0–3 eV [48], so that the IONs are semiconductor materials and they can be explored in optical sensor device applications. The band gap energy of Fe_3O_4 NPs has been reported in the range of 2.0–2.87 eV by earlier work [49].

As doping ionic radii increase, direct and indirect band gaps increase as can be shown from Table 1. The estimated direct and indirect band gap values of RE:SPIONs (RE = Dy, Nd, La) are found in the range of 3.2–3.55 eV and 1.1–1.25 eV respectively. These samples may contain visible light photo-catalytic activity because their indirect band gap value lies within the range of 1–3 eV [36]. It seems that the increase in both kinds of the optical energy gaps happens with the increase in the crystallite size [50,51] or in the other words, with the increase in ionic radii of rare earth dopants. The RE^{3+} ions which substitute Fe^{3+} ions may have energy levels shifting the Fe^{3+} energy levels away and consequently increase the energy band gaps. This view is supported by observing shift of the absorbance peak towards the lower wavelength (higher photon energy) values as shown in Fig. 4 and Table 1.

3.3 Magnetic properties

The magnetic hysteresis loops for SPIONs and RE:SPIONs at room temperature are given in Fig. 7. The magnetic parameters such as the saturation magnetization (M_s), remanence (M_r), and coercivity (H_c) determined by the hysteretic loops are listed in Table 2. From data of Table 2, M_s values of all the investigated samples range from 41.8 to 52.3 emu/g, which are consistent with other previous results [28,52,53] for IONs doping with rare earth ions. As can be observed from Table 2, the weak coercivity H_c of hysteresis loop (in the range of 28.2–46.3 G) and consequently negligible remanence M_r (in the range of 0.8–1.2 emu/g) indicate the superparamagnetic nature of the investigated samples. This could be due to the size of iron oxide-based nanoparticles, which is below the critical one of 25 nm for the formation of magnetic domains inside particle [54,55]. These magnetic data of the Dy, Nd, and La doped SPIONs exhibit higher M_s as compared with those reported in the literature for rare earth ions (Sm^{3+} , Eu^{3+} , Gd^{3+} ,

Fig. 7 Hysteresis loops of the SPIONs and RE:SPIONs samples.

Table 2 Saturation magnetization (M_s), remanence (M_r), and coercivity (H_c) of the SPIONs and RE:SPIONs samples

Sample	M_s (emu/g)	H_c (G)	M_r (emu/g)
Fe_3O_4	46.2	29.5	0.8
Dy: Fe_3O_4	45.9	28.2	0.9
Nd: Fe_3O_4	52.3	30.6	0.8
La: Fe_3O_4	41.8	46.3	1.2

Ho^{3+}) doped Fe_3O_4 powder [56–58]. For example, De Silva *et al.* [56] reported that the M_s values for $Sm:Fe_3O_4$ and $Eu:Fe_3O_4$ particles are 42.1/31.3 and 29.8/23.6 emu/g at 60/300 K, respectively.

It can be observed from Fig. 7 that, the value of M_s for SPIONs is high as compared to the Dy^{3+} :SPIONs and La^{3+} :SPIONs. This means that, replacement of Fe^{3+} ions from the octahedral sites by the RE^{3+} (Dy^{3+} and La^{3+}) ions [2,21,40] is led to decreasing the saturation magnetization of ferrites, which is similar to the reported results of RE doped ferrites [59–64]. The decrease in M_s of RE:SPIONs may therefore appear to be the consequence of many factors: a decrease in long range magnetic ordering upon insertion of large RE^{3+} ions into the Fe_3O_4 matrix, an increase in magnetic anisotropy, a decrease of the Fe^{3+} – Fe^{3+} interactions due to the reduction in the concentration of Fe ions on the B-sites [8,65,66]. La:SPIONs has the smallest value of M_s , as it can be shown from Table 2, where La^{3+}

ions are considered as paramagnetic (has no electrons in 4f orbit [67]) and make no contribution to the magnetization. Therefore, when the paramagnetic La^{3+} ions [67] replace the Fe^{3+} ions at B-site [2,10], it leads to decreasing the magnetic super exchange interactions A–B at tetrahedral and octahedral sites [68].

Our result upholds the fact that the secondary phase NdFeO_3 in Nd:SPIONs sample has led to increase in M_s value in comparison to Fe_3O_4 , Dy:SPIONs, and La:SPIONs samples. This result can be explained as following: the individual dipole in the ferromagnetic secondary phase (NdFeO_3) also aligns them in the direction of applied external magnetic field [69], and this may leads to increase of M_s . The remanence of the SPIONs and RE:SPIONs samples has the same trend of the crystallite size, which indicates to the strong relation between remanence and crystallite size of the samples. The superparamagnetic behavior of the investigated samples means that the thermal energy can overcome the anisotropy energy barrier of single IONs [70], and the coercivity and remanence of Fe_3O_4 nanoparticles are approaching zero in the absence of external field.

3.4 Dielectric properties

Figure 8 and Fig. 9 show the variation of dielectric constant ϵ' and dielectric loss ϵ'' of the SPIONs and RE:SPIONs samples as a function of the frequency in the range from 1 kHz to 1 MHz at room temperature. It can be observed that all the SPIONs and RE:SPIONs samples exhibit dielectric dispersion where the values of both ϵ' and ϵ'' decrease rapidly with increasing of the frequency, and at higher frequencies, they decrease slowly without any anomalous behavior or peaking behavior and tend to reach constant values. This character of dielectric parameters can be explained in the basic of hopping charge model and space charge polarization. The larger value of ϵ' at lower frequencies is mainly due to the contributions from polarizations of interfacial and space charge which are due to the inhomogeneous structure as suggested by Maxwell and Wagner [71,72]. Koops theory [73] suggests that ferrite system consists of a combination of highly conducting grains separated by poorly conducting grain boundaries. The contribution of the charge carriers to the dielectric constant decreases with the frequency increase. The dielectric constant reaches a constant value at high frequencies due to the fact that beyond a certain frequency of the

Fig. 8 Dielectric constant ϵ' of the SPIONs and RE:SPIONs samples versus logarithm of angular frequency.

Fig. 9 Dielectric loss ϵ'' of the SPIONs and RE:SPIONs samples versus logarithm of angular frequency.

external field, the electron exchange between Fe^{3+} and Fe^{2+} ions cannot follow the changes in the applied field [74]. Figure 8 shows that the dielectric constant of the RE:SPIONs decreases with the increasing of ionic radii of the dopants. The presence of rare earth ions inside lattice leads to the screening effect, which inhibits the motion of electrons between Fe^{2+} and Fe^{3+} where the mechanism of dielectric polarization is similar to that of conduction that depends on the charge carriers and thereby decreases the dielectric constant. In addition, there is a variation in dielectric constant which is directly proportional to the number of unpaired 4f electrons in the dopant ions. The dielectric constant increases for (La, Nd, Dy):SPIONs, where La, Nd, and Dy have zero, four, and five unpaired electrons in 4f level respectively [67,36,75].

3.5 Transport properties

3.5.1 AC conductivity

The variation of σ_{AC} with angular frequency ω is shown in Fig. 10 for all the SPIONs and RE:SPIONs samples. The plots are linear for almost entire range of frequency. Linear variation of σ_{AC} with frequency may be assigned to the hopping of charge carriers between the localized states on octahedral lattice sites which confirms the small polaron type of conduction

Fig. 10 AC conductivity of the SPIONs and RE:SPIONs samples versus logarithm of angular frequency.

[76,77]. The AC conductivities of SPIONs and RE:SPIONs increase with increasing the frequency. The increase in the frequency of the applied field accelerates the hopping of charge carriers, and the rate of hopping of charge carriers between Fe^{2+} and Fe^{3+} ions increases [78,79], resulting in an enhancement in the overall conduction process, thereby increasing the conductivity. AC conductivities of RE:SPIONs decrease with the increasing of ionic radii of rare earth RE^{3+} ions, where the RE^{3+} ions, with larger ionic radius entry to the octahedral sites instead of Fe^{3+} , maybe lead to increasing the separation between Fe^{2+} and Fe^{3+} ions and consequently, cause decrease to the hopping rate of electrons between them and decrease the AC conductivity.

3.5.2 DC conductivity

The variation of DC conductivity with temperature is shown in Fig. 11. The dependent electrical conductivity of the all samples on temperature shows semiconducting nature, which agrees with the energy gap values. The conduction mechanism of these samples is explained on the basis of Verwey and de-Boer [80], according to which the mechanism involves exchange of electrons between the cations of the same elements that are present in more than one valence state distributed randomly over crystallography lattice. That is, the conduction in these samples is attributed to hopping of electron from Fe^{2+} to Fe^{3+} ions. The increase of conductivity with the increase of temperature is due to the increase in drift mobility of the charge carriers. In fact, the mobility of electron is temperature dependent and is characterized by activation energy [81]. Activation energy in ferromagnetic region and paramagnetic region of SPIONs and RE:SPIONs is studied from the plot of $\ln \sigma$ versus $10^3/T$ as shown in

Fig. 11 DC conductivity of the SPIONs and RE:SPIONs samples as a function of temperature.

Fig. 11; the values are entered in Table 3. The variation of DC conductivity with respect to temperature follows the Arrhenius law: $\sigma = \sigma_0 \exp(-E_a / k_B T)$, where σ_0 is a pre-exponential factor, k_B is Boltzmann constant, and T is absolute temperature [82]. The plot of $\ln \sigma$ versus $10^3/T$ for each sample shows a break at certain temperature T_c , giving two distinct regions with different slopes. In Fig. 11, each sample shows a break near the transition temperature and is attributed to the transition from ferromagnetic region to paramagnetic region with two slopes or activation energies. The two slopes are because of change of conduction mechanism before and after the transition temperature ($T_c = 352$ K). The electrons in SPIONs sample are localized and there is lattice overlap between the wave functions of ions situated on the adjacent sides. As the temperature increases, the lattice vibration increases and then the ions occasionally come close, thus the transfer of the electrons from one ion to another ion also increases, and this means that as temperature increases the mobility of hopping electrons increases as well as conductivity [78]. The calculated values of activation energies are listed in Table 3. It can be shown that, the activation energies in paramagnetic region (E_{a1}) are higher than those in ferrimagnetic region (E_{a2}). Moreover, the change of activation energies can be attributed to the change of conduction mechanism from polaron to hopping [83]. The lower activation energies (E_{a2}) are attributed to magnetic disordering owing to limited availability of charge carriers [84]. Also, it can be observed from Fig. 10 and Table 3 that, the DC conductivity decreases and the activation energies increase in the RE:SPIONs with the increasing of ionic radii of rare earth RE^{3+} ions. This can be explained as following: when the RE^{3+} ions with larger ionic radius entry to the octahedral

Table 3 Activation energies of the SPIONs and RE:SPIONs samples

Sample	E_{a1} (eV)	E_{a2} (eV)
Fe ₃ O ₄	0.283	0.367
Dy _{0.05} Fe _{2.95} O ₄	0.279	0.291
Nd _{0.05} Fe _{2.95} O ₄	0.278	0.294
La _{0.05} Fe _{2.95} O ₄	0.345	0.371

sites of Fe₃O₄ lattice maybe cause decrease to the hopping rate of electrons due to enhancing the separation between Fe²⁺ and Fe³⁺ ions and consequently, decrease the DC conductivity and enhance the activation energies.

4 Conclusions

SPIONs and RE:SPIONs were synthesized by co-precipitation technique. The X-ray patterns of Dy:Fe₃O₄ and La:Fe₃O₄ samples have a single phase of Fe₃O₄, whereas Nd:Fe₃O₄ sample has phase patterns of Fe₃O₄ structure with a few amount of secondary phase corresponding to NdFeO₃. Both the lattice constant and lattice strain decrease, whereas the crystallite size increases with increasing ionic radii of the dopants. SEM images of all the SPIONs and RE:SPIONs samples show that the particles have a spherical like shape in nanosize with agglomeration. The saturation magnetization M_s has values in the range from 41.8 to 52.3 emu/g. The secondary phase NdFeO₃ in Nd:Fe₃O₄ sample leads to increase in the saturation magnetization value in comparison to Fe₃O₄, Dy:Fe₃O₄, and La:Fe₃O₄ samples. The very weak coercivity H_c (28.2–46.3 G) and negligible remanence M_r (0.8–1.2 emu/g) values, indicate the superparamagnetic nature of the investigated samples. The absorbance wavelength peak of undoped Fe₃O₄ is higher than that of doped Fe₃O₄. Where RE dopant ions reduce oxidation of Fe₃O₄ SPNs and with the calculated values of saturation magnetization and crystallite size and spherical shape, nanoparticles can be explored in drug delivery applications. The calculated direct and indirect optical band gap values of pure Fe₃O₄ samples are 2.25 and 0.9 eV respectively. Both the direct and indirect band gap values of RE:Fe₃O₄ are in the range of 3.2–3.55 and 1.1–1.25 eV respectively. The calculated values of indirect optical band gap of Fe₃O₄ and RE:Fe₃O₄ nanoparticles indicate that these samples are semiconductor materials and they can contain visible

light photocatalytic activity, so they may be candidate for optical sensor device application. The dielectric constant of SPIONs decreases and the activation energies increase with the increasing of ionic radii of the dopants.

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