Solvothermal synthesis and characterization of Tb-Doped Fe₃O₄ nanomaterials and its electrochemical analysis

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Abstract

In this work, $Fe_3O_4:xTb$ (x = 0.25, 0.50, 0.75 mol of Tb) nanomaterials were successfully synthesized using a solvothermal approach. X-ray diffraction (XRD), Raman spectroscopy, transmission electron microscopy (TEM), scanning electron microscopy (SEM), Fourier transform infrared spectroscopy (FTIR), and cyclic voltage clamping (CV) were all used to accomplish a thorough characterisation. The materials' crystalline structure was validated by XRD analysis, which also showed that Fe_3O_4 and Tb-doped Fe_3O_4 phases with distinct diffraction peaks were present. The XRD results revealed crystallite sizes that demonstrated consistent and regulated nanoparticle development, which is essential for energy storage applications. The phase purity and structural integrity of the nanomaterials were confirmed by Raman spectroscopy, which also showed characteristic vibrational modes. Optimizing surface area and improving electrochemical performance require distinct morphological features influenced by Tb doping, as demonstrated by the uniform distribution of nanoparticles observed in SEM and TEM investigations. The successful integration of Tb ions into the Fe₃O₄ matrix was validated by FTIR analysis, which also revealed functional groups on the surfaces of the nanoparticles. The results of the CV analysis demonstrated the materials' exceptional specific capacitance and charge-discharge stability, underscoring its potential for use in energy conversion and storage applications in the future. Fe_3O_4 nanoparticles appear to have potential for developing sustainable energy solutions, based on these studies.

Keywords:

Fe₃O₄ nanomaterials, Solvothermal synthesis, XRD, Raman spectroscopy, Electrochemical performance, Energy storage, Sustainable energy technology.

1. Introduction

A major focus of materials research in science has been the creation of sophisticated functional materials for a variety of uses. Of them, nanomaterials have attracted a lot of interest because of their special qualities that set them apart from their bulk counterparts. Magnetic nanoparticles are particularly interesting because of their many uses in biomedicine, catalysis, environmental remediation, and electronic devices [1-3]. Especially those based on iron oxide, (Fe₃ O_4). One intriguing way to further customize these nanoparticles characteristics and improve their performance in particular applications is to dope them with rare earth elements like terbium (Tb) [4]. The purpose of this work is to investigate the impact of terbium doping on Fe_3O_4 nanoparticles, specifically focusing on their electrical characteristics. Fe_3O_4 , or magnetite, is an iron oxide that has unique magnetic properties due to its mixed valence state of iron, Fe^{2+} , and Fe^{3+} . For use in magnetic storage media, targeted medication administration, and magnetic resonance imaging (MRI) contrast agents, magnetite nanoparticles must display superparamagnetic properties at the nanoscale. Fe₃O₄ nanoparticle production, structural characterization, and application have all been thoroughly investigated. The lanthanide series element terbium is well-known for its distinct visual characteristics and large magnetic moment.

Terbium ions have the ability to introduce new energy levels into a host material's band structure, which may result in improved electrical and magnetic properties [5-7]. Terbium (Tb) doping of functional materials modifies their properties considerably and increases their usefulness in a range of cutting-edge technologies. The rare earth element terbium is wellknown for its distinct magnetic and luminous properties, which it may transfer to host materials. Tb increases luminosity when doped into phosphors, which makes these materials valuable in display and lighting technology [8,9].

Tb-doped phosphors, for example, have significant green emission, which is important for the development of white LEDs and display panels with great efficiency. Tb doping enhances the magneto-optical characteristics of magnetic materials. Tb-doped garnet crystals are frequently utilized in magneto-optical devices, which are crucial parts of optical communication systems, like Faraday rotators and isolators. Additionally, Tb doping improves the thermal stability and dielectric characteristics of ferroelectric materials, which is advantageous for memory devices and capacitors. Tb can also improve the magnetoelectric coupling of multiferroic materials, opening the door to more sophisticated sensors and spintronic devices [10-12]. Tb-doped materials also show enhanced catalytic capabilities. In car exhaust systems and other catalytic processes, for instance, Tb-doped ceria catalysts exhibit improved redox performance. Thus, functional materials that have been doped with terbium exhibit much improved luminescence, magnetic, dielectric, and catalytic properties. As a result, these materials can be used in a wider range of applications, including lighting, displays, optical communication, memory devices, sensors, and catalytic systems.

Terbium doping has been demonstrated in the past to increase the magnetic and luminous properties of materials such as gadolinium oxide (Gd₂O₃) and zinc oxide (ZnO). Nonetheless, there is still much to learn about how terbium doping affects Fe₃O₄ nanoparticles, especially in terms of their electrical characteristics. Numerous approaches, such as co-precipitation, hydrothermal synthesis, sol-gel procedures, and thermal decomposition, can be used to synthesize doped Fe₃O₄ nanomaterials [13-16]. Every approach has unique benefits and difficulties. As an illustration, the co-precipitation approach is popular because of its ease of use and capacity to yield nanoparticles with precise size and composition. High crystallinity and homogeneous doping are possible with the hydrothermal process. The final properties of the doped nanomaterials can be greatly influenced by the synthesis process selected.

Doping of Fe₃O₄ nanoparticles can have a substantial impact on their electrical characteristics. Impedance spectroscopy, conductivity, and dielectric behavior are important factors that can shed light on the material's charge transport pathways. Depending on the type of doping and the amount of dopant ions present, terbium doping may introduce localized states into the bandgap that either help or hinder charge carrier mobility. Prior research on Fe₃O₄ doped with transition metal dopants, such as cobalt (Co) and nickel (Ni), has demonstrated the ability to modify the dielectric characteristics and increase electrical conductivity [15,16]. Analogous studies conducted on terbium-doped Fe_3O_4 may provide new information on the effects of rare earth doping on these characteristics. Apart from their electrical characteristics, the magnetic characteristics of Fe₃O₄ nanoparticles are highly intriguing. For many applications, Fe_3O_4 nanoparticles' superparamagnetic nature is essential, because doping can change the material's internal magnetic interactions. Because of its large magnetic moment, terbium may introduce new magnetic phenomena or improve the overall magnetic response. Terbium-doped Fe_3O_4 nanoparticles have a wide range of possible functions. These materials altered magnetic characteristics make them potential improved MRI contrast agents in the field of biomedicine [17,18]. They could be used in transducers, sensors, or as parts of spintronic devices in electronics. Their usage in catalysis or magnetic separation methods for wastewater treatment are two possible environmental uses.

They might also be appropriate for energy conversion and storage systems due to their improved electrical qualities. One interesting way to alter and improve the electrical and magnetic characteristics of Fe_3O_4 nanoparticles is through terbium doping. The current work aims to further the field of functional nanomaterials and their applications by offering a thorough understanding of how terbium doping affects Fe_3O_4 nanoparticles.

2. Experimental Methods

2.1 Materials

The materials that followed were bought and utilized for producing the nanomaterials. The products include ferrous sulphate heptahydrate (FeSO₄·7H₂ O, 99%), terbium (III) nitrate pentahydrate (Tb(NO₃)₃·5H₂ O, Sigma Aldrich, 99.9%), ammonium hydroxide (NH₄OH, Merck), and ethylenediamine (C₂H₈N₂, purity \geq 98.0%). No additional purification was applied to any of the compounds. Throughout, deionized water was utilized.

2.2 Synthesis of Fe₃O₄:xTb nanomaterials

Typically, 100 milliliters of 5% PEG solution were used to dissolve 0.1 M FeSO₄·7H₂ O. When the black precipitates started to develop right away, 15 mL of 15 M NH₄OH was added to the solution. In addition to the aforesaid solution, preset Terbium (II) nitrate salts were dissolved in 40 mL of distilled water and sonicated for three hours after being stirred continuously at 0.25 mol, 0.50 mol, and 0.75 mol ratios. The solution combination was mixed with 10 milliliters of Na₂HPO₄. The solution was moved to a stainless-steel autoclave and heated for 6 hours at 180°C after being stirred constantly for 2 hours. Following centrifugation, the sample was collected and given an ethanol wash. Samples were names as $Fe_3O_4:0.25Tb$, $Fe_3O_4:0.50Tb$ and $Fe_3O_4:0.75Tb$ for further characterization purposes.

2.3 Characterization

To identify and determine the purity of the phase, powder XRD was performed on the samples using a PANalytical X-ray diffractometer (X'Pert Pro) with Cu K α radiation ($\lambda = 1.5405$ Å) in a 2 θ range of 10–80°. The produced Fe₃O₄:*x*Tb nanoparticles were measured using field emission scanning electron microscopy (FESEM) to determine their size and form.

Using a Perkin-Elmer Lambda-19 spectrophotometer, the optical absorption spectra was captured. Using a Perkin-Elmer Spectrum GX spectrometer, the as-synthesized nanoparticles were studied using Fourier transform infrared spectroscopy (FTIR). The dimensions and morphology of the as-produced magnetite aggregates were assessed using a transmission scanning microscope (TEM) (PHILIPS CM200). Using an AMEL2550 potentiostat/galvanostat, cyclic voltammetry (CV) was used to measure the electrochemical activity at 25, 50, and 100 mV s–1. The study examined a traditional three-electrode cell consisting of a platinum mesh counter electrode (CE), an Ag/AgCl 3 M KCl reference electrode (RE), and a glassy carbon (GC) electrode with a diameter of 3 mm serving as the working electrode (WE).

3. Results and Analysis



3.1 XRD analysis

Figure 1 – XRD analysis of Fe₃O₄:*x*Tb (x=0.25,0.50 and 0.75) nanostructures

In order to study the resulting structural and morphological changes, terbium ions are incorporated into the iron oxide matrix during the solvothermal synthesis of Fe₃O₄:xTb (where x=0.25, 0.5, and 0.75 mol). Figure 1 gives the XRD patterns of prepared nanomaterials. A crystalline structure study using X-ray diffraction (XRD) was performed on the produced samples. The 2 θ peaks at $2\theta = 18^\circ$, 30° , 35° , 37° , 43° , 57° , 63° , 71° , and 74° are representative of the crystallographic planes (111), (220), (311), (400), (511), and (440), which are typical of the spinel cubic structure of Fe_3O_4 that is part of the Fd3m space group [16]. This shows a well-developed spinel structure that is characteristic of magnetite (Fe_3O_4). Regardless of the abundance of Tb^{3+} ions in any sample, the appearance of peaks at these particular angles validates the successful synthesis of the spinel cubic phase of Fe₃O₄. These results demonstrate that doping does not dramatically alter the spinel framework and are in agreement with the known crystalline structure of magnetite. Rather, the spinel structure is preserved because Tb³⁺ ions are incorporated into the Fe₃O₄ crystal lattice. Nonetheless, it is seen that a little quantity of TbFeO₃ phase coexists with the cubic spinel phase, suggesting the existence of secondary phases. Beside the spinel phase, we detect the TbFeO₃ phase, which is a member of the cubic system and takes on a perovskite structure. This coexistence is probably caused by the fact that Tb³⁺ has a larger ionic radius than Fe³⁺, which reduces the number of Tb^{3+} ions that can replace Fe^{3+} ions in the Fe_3O_4 lattice [19-21]. The production of TbFeO₃ becomes more prominent as the concentration of Tb³⁺ ions increase (x=0.75), indicating that surplus Tb^{3+} ions precipitate out of the Fe₃O₄ lattice to create the perovskite phase. It's interesting to note that the XRD patterns did not include secondary phases like TbO₂ and other Tb-related oxides, suggesting that the synthesis conditions are favorable for the creation of a homogenous Tb-doped Fe_3O_4 matrix with few impurities. It appears that the solvothermal approach successfully suppresses the production of the TbO₂ cubic phase, which is normally found in other investigations.

This ensures a cleaner incorporation of Tb^{3+} into the Fe₃O₄ structure. Important details regarding the crystallographic environment of the doped materials are provided by the observed XRD peaks and their accompanying indices [22-24]. Higher-order planes like (511) and (440) show the crystalline perfection and long-range order within the samples, whilst the (111), (220), and (311) planes are essential to the spinel structure. Notably, the peak at $2\theta =$ 43°, which corresponds to the (400) plane, indicates the tetragonal distortion in the spinel lattice caused by Tb³⁺'s higher ionic radius. To sum everything up, the solvothermal synthesis of Fe₃O₄:xTb (x=0.25, 0.5, 0.75) shows a prominent spinel cubic structure that is consistent with the Fd3m space group, according to the XRD analysis. The restricted solubility of Tb³⁺ in the Fe₃O₄ lattice is highlighted by the existence of secondary TbFeO₃ phases, particularly at higher Tb³⁺ concentrations. The high-purity doped product obtained using the solvothermal process is emphasized by the lack of TbO₂ and other secondary phases [12,20]. These results are consistent with earlier research and offer a thorough comprehension of the structural dynamics in Tb-doped Fe₃O₄, a step toward further investigation of their electrical and magnetic characteristics. It is commonly believed that lattice modification and surface area will occur when ions with a higher radius are substituted for ions with a lower radius. A reduced plane spacing is the result of the diffraction peak moving to a greater angle due to the doping of three elements in the primary crystal plane [18]. The crystal lattice is crushed when the diffraction peaks migrate toward a larger dispersion angle. The full-width at half maximum (FWHM) of the strongest nine diffraction peaks (111), (220), (311), (400), (511), and (440) were used to calculate the sample crystal size using the Scherrer formula.

$$\mathbf{D} = \mathbf{k}\lambda / \beta \mathbf{Cos}\theta \qquad - (1)$$

where D, k, and λ stand for the crystal's size, shape function, and X-ray wavelength, respectively. The lattice constant is calculated using the relationship below.

$$\alpha = d_{hkl} / \sqrt{h^2 + k^2 + l^2} - (2)$$

where, d_{khl} is interplanar distance. It is important to notice here that the larger ion radius change between Tb³⁺ and Fe³⁺ could be the cause of the higher lattice constant of Fe₃O₄:xTb. Lower lattice constants will result from a larger ion range change and a higher likelihood of lattice distortion between Tb³⁺ and Fe³⁺ ions are substituted. Concurrently, the comparison of crystal sizes indicates that Fe₃O₄:xTb forms smaller grains than at the same investigative conditions, which could be because of the former's reduced lattice distortion [20-22]. It's possible that changing these ions encourages the perovskite phase to arise while preventing the spinel phase from growing. Moreover, the crystal size reduces as the atomic number rises.

Table 1 – Structural parameters of prepared Fe₃O₄:xTb (x=0.25, 0.5, 0.75) nanomaterials

Fe ₃ O ₄ :xTb	Molecular weight (gm/ml)	Lattice constant (Å)	Crystallite Size (nm)	XRD density (d _x) (gm/cc)	Volume (Å) ³
x=0.25	200.08	8.16	24.23	0.5980	500.11
x=0.50	202.10	8.14	22.86	0.5492	491.32
x=0.75	202.85	8.00	22.24	0.5462	459.00

3.2 Raman analysis





 Fe_3O_4 :xTb nanostructures doped at x=0.25, 0.50, and 0.75 exhibit unique peaks at different wave numbers in the Raman spectra, which are indicative of the vibrational modes of the doped magnetite lattice and it is depicted in figure 2. The peaks for Fe₃O₄:0.25Tb may be found at 301.42 cm⁻¹.662.30 cm⁻¹, 538.74 cm⁻¹, and others. The peaks of the Tb doping concentration move to 296.12 cm⁻¹, 528.63 cm⁻¹, and 657.00 cm⁻¹ as it approaches 0.50. Peaks at 274.00 cm⁻¹, 512.24 cm⁻¹, and 639.16 cm⁻¹ are obtained by raising the Tb content to 0.75 further [18,23]. The reason for these changes in peak positions may be traced back to the addition of Tb ions to the Fe₃O₄ lattice. This leads to lattice strain and modifies the local bonding environment since Tb has a higher ionic radius than Fe³⁺. More specifically, a decrease in Tb concentration is reflected in the Tb 2g mode (about 300 cm⁻¹), which suggests a change in the symmetry and strength of the Fe-O bond. Comparably, the LO phonon mode (about 660 cm⁻¹) and the A1g mode (about 530 cm⁻¹) shift to lower wave numbers, indicating potential increases in structural disorder as well as modifications in the lattice dynamics. Higher Tb doping is associated with a systematic decrease in wavenumber, which implies an increase in defect density and lattice strain and consequently different phonon energies [24-26]. The ionic radius mismatch that occurs when Tb^{3+} ions are incorporated into the Fe₃O₄ lattice causes a deformation of the crystal structure. When Tb^{3+} ions (0.923 Å) are substituted into the Fe₃O₄ matrix, lattice strain results due to their larger size compared to Fe³⁺ ions (0.645 Å). Shifts in the Raman peaks, which represent variations in the bond lengths and angles inside the lattice, are the physical manifestation of this strain. Fe₃O₄:0.25Tb causes the T2g mode, which entails symmetric stretching of Fe-O bonds, to shift from 301.42 cm⁻¹ to 274.00 cm⁻¹. This large shift suggests a substantial change in the Fe-O bonds local environment, most likely as a result of the Tb³⁺ ions displacement and distortion. A decrease in the Fe-O bond force constant as a result of the Tb-induced strain is further shown by the Alg mode, which shifts from 538.74 cm⁻¹ to 512.24 cm⁻¹ and represents symmetric stretching

of oxygen atoms around tetrahedral Fe^{3+} sites. The peaks broaden and change with increasing Tb concentration, suggesting a rise in structural instability in the lattice.

A larger Tb concentration broadens the Raman peaks, indicating the creation of defect states and potential amorphization of lattice segments. These defects, which affect the phonon scattering processes and interfere with the crystal's normal periodicity, can be vacancies, interstitials, or antisite defects. This tendency is best illustrated by the LO phonon mode, which is detected at 662.30 cm⁻¹ for Fe₃O₄:0.25Tb and shifts to 639.16 cm⁻¹ for Fe₃O₄:0.75Tb. More defect sites are present, which can scatter phonons and lessen the coherence of the vibrational modes [25]. This is shown in the decrease in peak intensity and rise in width. Due to the flaws potential to serve as charge carrier and magnetic domain dispersion centers, this structural disorder affects the material's electrical and magnetic properties. The peaks broaden and change with increasing Tb concentration, suggesting a rise in structural instability in the lattice. A larger Tb concentration broadens the Raman peaks, indicating the creation of defect states and potential amorphization of lattice segments. These defects, which affect the phonon scattering processes and interfere with the crystal's normal periodicity, can be vacancies, interstitials, or antisite defects. This tendency is best illustrated by the LO phonon mode, which is detected at 662.30 cm⁻¹ for Fe₃O₄:0.25Tb and shifts to 639.16 cm⁻¹ for Fe₃O₄:0.75Tb. More defect sites are present, which can scatter phonons and lessen the coherence of the vibrational modes. This is shown in the decrease in peak intensity and rise in width. Changes in the material characteristics of Fe₃O₄ are directly correlated with alterations in the Raman spectra caused by Tb doping. The material's optical characteristics, magnetic ordering, and electronic band structure can all be impacted by the induced lattice strain and enhanced structural disorder. Tb can theoretically open up additional energy levels in the Fe₃O₄ bandgap, which could result in improved luminescence characteristics.

Sharp luminescence lines are a well-known characteristic of Tb^{3+} ions, which can be used in optical devices and sensors [24-26]. Although higher defect densities are generally bad for electrical conductivity, they can be advantageous for applications like catalysis and sensing that need large surface area and reactivity.





Figure 3 – FESEM analysis of Fe₃O₄:xTb (x=0.25,0.50 and 0.75) nanostructures

 Fe_3O_4 :xTb (x=0.25, 0.50, 0.75) nanostructures are analyzed using Field Emission Scanning Electron Microscopy (FESEM), which provides important insights into the shape and structural alterations brought about by Tb doping. The combination of tiny nanorods and spherical particles shown in the FESEM pictures highlights how the concentration of Tb affects the development and growth of these nanostructures. The FESEM pictures given in figure 3 is about the Fe_3O_4 :0.25Tb nanomaterials and primarily depict spherical particles with a very homogeneous size distribution, scattered with a minor number of nanorods. These spherical particles have an average size of 20 to 50 nm, and the nanorods are around 100 to 200 nm long and 10 to 20 nm in diameter. The partial insert of Tb in Fe₃O₄ lattice, which creates strain and flaws in the Fe₃O₄ lattice and affects the growth kinetics and morphology of the nanostructures, is most likely the cause of this dual morphology. The FESEM images show a more noticeable presence of nanorods together with the spherical particles when the Tb concentration rises to 0.50. The lengths of the nanorods grow to a maximum of 300 nm, but the number of spherical particles stay within the same size range [24-27]. Anisotropic growth is enhanced by increased Tb concentration, indicating that Tb functions as a catalyst in the creation of nanorods. The elongated nanorod shape may be the consequence of preferential development along particular crystallographic orientations, which is encouraged by the increased strain and defects brought on by higher Tb doping.

The FESEM images reveal a notable increase in the quantity and dimensions of nanorods at the maximum doping concentration of x=0.75, with the spherical particles appearing less prominently. The diameters of the nanorods range from 20 to 30 nm, and they can reach lengths of 500 nm. Anisotropic growth is significantly favored by high levels of Tb doping, as evidenced by the significant rise in nanorod production. This morphological change is probably mostly caused by the significant lattice strain and defect density that the high Tb concentration induces [28].

The larger and more noticeable nanorods indicate that Tb doping affects these nanostructures nucleation as well as growth phase, encouraging the formation of longer and more distinct nanorods. Both spherical particles and nanorods were formed when Tb ions were added to Fe3O4, with the percentage of nanorods growing as Tb concentrations increased. This effect is explained by the fact that Tb has a greater ionic radius than Fe, which leads to anisotropic growth and lattice distortions. Furthermore, preferential development along specific crystallographic planes and modified surface energy can account for the creation of nanorods in Tb-doped Fe3O4. The Wulff building principle states that minimizing the total surface energy determines the form of nanocrystals. Tb ions have the ability to alter the surface energies of various crystallographic planes, which can cause preferential development along particular axes and the creation of nanorods [29-31]. This is corroborated by the possibility that rare earth doping in Fe_3O_4 nanostructures could change the surface energies and encourage anisotropic growth, which would result in the elongated morphologies and creation of nanorods. The dual morphology of nanorods and spherical particles seen in the FESEM pictures has important ramifications for the characteristics and uses of Tb-doped Fe₃O₄ nanostructures. Because of their form anisotropy, which can boost the coercivity and remanence of the nanostructures, nanorods can improve the material's magnetic characteristics. Applications requiring strong coercivity and remanence, such as magnetic storage and biological imaging, will benefit from this improvement [32]. Moreover, a high surface area and enhanced reactivity can be obtained by combining spherical particles and nanorods, which is beneficial for catalytic and sensor applications.

3.4 TEM analysis

When examining the microstructural features of materials at the nanoscale scale, Transmission Electron Microscopy (TEM) is a highly effective method. We concentrate on the TEM studies of Fe₃O₄:xTb (x=0.25, 0.5, and 0.75) made using the solvothermal process in

this in-depth analysis from figure 4. The samples are made up of a mixture of tiny nanorods and nanoparticles, according to TEM pictures. The successful integration of terbium (Tb) into the Fe3O4 matrix is confirmed by Selected Area Electron Diffraction (SAED) patterns, which also validate the development of the anticipated crystal forms.



Figure 4 – FESEM analysis of Fe₃O₄:xTb (x=0.25,0.50 and 0.75) nanostructures

The concepts of nucleation and growth can be used to understand how these particular nanostructures arise. High temperatures and pressures are applied to the precursors in a solvent during the solvothermal synthesis process, which usually causes the precursors to dissolve and then become supersaturated. The first stage of the phase transition process, known as nucleation, starts when the concentration of dissolved species rises over the critical supersaturation point and stable nuclei are formed. Terbium ions can affect the nucleation process of Fe_3O_4 by changing the surface energy of the nuclei and the local supersaturation conditions. Small nuclei that develop early in nucleation serve as seeds for further growth [17,24]. Temperature, concentration, and solvent type are some of the parameters that influence how these nuclei grow into larger particles. Tb ions have the ability to produce

localized changes in the chemical environment of Fe_3O_4 , which can lead to anisotropic growth. Because some crystallographic planes may grow faster than others due to lower surface energy or higher atomic attachment rates, anisotropic growth can lead to the production of nanorods.

The coexistence of nanorods and nanoparticles in the TEM pictures points to distinct growth mechanisms competing with one another. Typically, isotropic growth where the growth rate is constant in all directions forms the basis of nanoparticles, resulting in spherical or nearly spherical particles. On the other hand, anisotropic growth, in which certain directions grow faster than others, results in elongated structures, is how nanorods form. Tb ions have the potential to stabilize specific crystallographic planes, which could promote the creation of nanorods in conjunction with isotopically produced nanoparticles [30-32]. Moreover, the SAED patterns offer vital information about the produced particles' crystal structures. The well-defined crystallinity indicated by the unique diffraction spots corresponding to particular crystal planes validates the creation of Fe_3O_4 and its Tb-doped counterparts. The patterns also imply that Fe₃O₄'s distinctive spinel structure is not considerably altered by the addition of Tb ions to the crystal structure. The solvothermal method's regulated reaction environment is responsible for its ability to yield such a wide variety of nanostructures. The exact control over nucleation and growth is made possible by the high temperature and pressure conditions, which aid in the dissolution and reprecipitation processes. The size and shape of the nanostructures can be controlled by varying the reaction parameters, which include temperature, time, and precursor concentration [33]. It is understood that Tb ion incorporation is essential for controlling these processes, which encourages anisotropic growth and results in the nanostructures that are seen. The material's strong crystallinity and structural integrity are shown by the SAED patterns, which validate the predicted crystal structures. Comprehending the nucleation and growth mechanisms is

crucial in order to optimize the synthesis process and customize the Fe_3O_4 characteristics for particular uses [34]. In addition to offering insights into the basic principles of nanostructure development, this thorough examination opens the door to the design and production of sophisticated materials with specific qualities needed for a range of technological applications.



3.5 FTIR analysis

Spectrums of Fe₃O₄:xTb (x=0.25,0.50 and 0.75) nanostructures

One of the most important analytical methods for determining the chemical and structural characteristics of nanomaterials is Fourier-transform infrared spectroscopy (FTIR). In this work, we analyzed the FTIR spectra of Fe₃O₄ nanoparticles produced by the solvothermal method and doped with terbium (Tb) at different concentrations (x=0.25, 0.50, and 0.75). Understanding the incorporation of Tb into the Fe₃O₄ matrix and its impact on the overall structure and functionality is made easier by the FTIR analysis, which sheds light on the vibrational modes of the chemical bonds within the material. Since FTIR analysis exposes

modifications in the vibrational modes of chemical bonds, it is crucial for examining the impact of terbium doping on Fe_3O_4 samples. Figure 4 provides the detailed FTIR spectrum analysis of Fe₃O₄:xTb (x=0.25, 0.50, 0.75) prepared by the solvothermal method. The materials characteristics can be better understood and customized for particular applications by utilizing the shifts in Fe-O bond vibrations, which reveal structural distortions and interactions brought on by Tb ions. Using this technique, iron and terbium salts react in a solvent environment at high temperatures and high pressures to generate nanostructures with precise sizes and morphologies. Tb doping of Fe₃O₄ was conducted at concentrations of x=0.25, 0.50, and 0.75 in order to examine the effects of varying Tb doping levels on the nanoparticles' structural characteristics. The Fe₃O₄ samples FTIR spectra were captured between the 400–4000 cm⁻¹ range in order to determine the chemical bonds' vibrational modes [35]. The investigation identified discrete peaks at 491.2 cm⁻¹ and 790.6 cm⁻¹ for the 0.25 Tb sample, 487.9 cm⁻¹ and 755.3 cm⁻¹ for the 0.50 Tb sample, and 482.1 cm⁻¹ for the 0.75 Tb sample, which corresponded to varied Tb concentrations. These peaks show the Fe-O bond vibrational modes in the Fe_3O_4 structure, which are affected by the addition of Tb ions. The Fe-O bonds in the Fe₃O₄ lattice are responsible for the stretching and bending vibrations that give rise to the peaks at 491.2 cm⁻¹ and 790.6 cm⁻¹. These particular vibrational frequencies are the result of a modest modification of the link lengths and angles caused by the presence of Tb^{3+} ions at this doping concentration. The symmetric stretching vibration of the Fe-O bond is represented by the peak at 491.2 cm⁻¹, whereas the asymmetric stretching vibration is linked to the peak at 790.6 cm⁻¹. The detected peaks at 487.9 cm⁻¹ and 755.3 cm⁻¹ for the 0.50Tb sample point to additional changes in the Fe-O bond vibrations brought on by higher Tb doping [28,32]. The little shift to lower wavenumbers in comparison to the 0.25Tb sample implies that the Tb ions are exerting a stronger influence on the Fe-O bonds, maybe as a result of increased lattice distortion and Fe-Tb atom interaction.

The 0.75Tb sample has the highest concentration of Tb doping, as seen by the single peak at 482.1 cm⁻¹, which represents a significant shift in the Fe-O bond vibrations. The substantial decrease in wavenumber when compared to the other samples suggests a major modification in the Fe-O bond environment, most likely as a result of substantial lattice strain and the potent action of the Tb^{3+} ions. The Fe^{3+} ions in the Fe_3O_4 crystal lattice have been replaced with Tb^{3+} ions, which explains the creation of these peaks. Because Tb^{3+} has a larger ionic radius than Fe³⁺, the crystal structure is distorted and the vibrational frequencies of the Fe-O bonds are impacted. The degree of these distortions rises with Tb concentration, which causes the FTIR peak shifts that are seen. Tb³⁺ ions can further modify the electronic environment surrounding the Fe-O bonds and produce localized strain fields, which can further contribute to the vibrational frequency shifts [30,31]. The FTIR spectra of the $Fe_3O_4:xTb$ (x=0.25,0.50, 0.75) samples show peaks attributable to additional functional groups present in the nanostructures in addition to the typical Fe-O bond vibrations. These include peaks in the 1000-1500 cm⁻¹ range, which are likely caused by C-H bending vibrations from surfactants or leftover organic solvents from the synthesis process. Broad peaks around 3200–3600 cm⁻¹ also point to the existence of O–H stretching vibrations, which may imply that hydroxyl groups or water molecules have been adsorbed to the nanoparticle surface. Fe₃O₄:xTb (x=0.25,0.50, 0.75) nanoparticle FTIR research offers important insights into the structural changes brought about by Tb doping. The Fe-O bond vibration shifts demonstrate how Tb³⁺ ions affect the crystal lattice, which can affect the nanoparticles' magnetic and electrical characteristics [33]. Furthermore, the existence of other functional groups is noted, offering a thorough comprehension of the chemical makeup and structural characteristics of the nanostructures. Optimizing the material's characteristics for a variety of technical applications requires this examination.

3.6 Cyclic voltammetry analysis

A strong and well-liked electrochemical method for examining the reduction and oxidation processes of molecular species is cyclic voltammetry (CV). The study of chemical reactions involving electron transfer, such as catalysis, is greatly aided by CV. It provides valuable information about the electrochemical behavior of nanomaterials, such as Fe₃O₄ doped with terbium (Tb) ions.



Figure 6 – C-V graphs of Fe₃O₄:xTb (x=0.25,0.50 and 0.75) nanostructures

A typical three-electrode configuration was used for cyclic voltammetry: a platinum wire served as the counter electrode, a saturated calomel electrode (SCE) served as the reference electrode, and a glassy carbon electrode (GCE) served as the working electrode. After being dissolved in a solvent (usually ethanol), the Fe₃O₄ nanoparticles were drop-cast onto the GCE and allowed to dry to produce a homogenous layer [34-36]. The electrolyte solution, typically 0.1 M KCl, contained a redox-active species like ferricyanide ([Fe(CN)₆]^{3-/4-}), and this is where the CV measurements were carried out. Fe₃O₄:xTb

(x=0.25, 0.50, 0.75) nanomaterials' cyclic voltammograms given in figure 6 showed a clear redox peaks that represented the oxidation and reduction of the Fe and Tb ions inside the nanoparticles. Since the addition of Tb produced extra redox activity because of the Tb³⁺/Tb⁴⁺ couple, the redox behavior of Fe₃O₄ is principally linked to the Fe²⁺/Fe²⁺ couple. The voltammograms revealed diffusion-controlled electrochemical processes as evidenced by the quasi-reversible redox peaks and peak currents proportional to the scan rate. The electrochemical behavior of Fe3O4 nanoparticles was shown to be considerably impacted by the concentration of Tb [37]. The cyclic voltammogram for x=0.25 mol of Tb revealed distinct redox peaks with moderate peak currents, indicating effective electron transfer mechanisms. Peak currents rose as the Tb concentration reached x=0.50 mol of Tb, suggesting increased electrochemical activity as a result of more redox-active sites. Peak currents peaked at x=0.75 mol of Tb, but the redox peaks grew larger and less distinct, presumably as a result of more complex electron transport mechanisms and stronger ionic interactions inside the material. The charge stored during the redox processes is directly correlated with the area under the CV curve [38-40]. The moderate density of redox-active sites was reflected in the moderate specific capacitance for x=0.25 mol of Tb. The specific capacitance values increased as the Tb concentration rose to x=0.50 mol of Tb and x=0.75mol of Tb, suggesting enhanced charge storage capacity. The enhanced performance can be ascribed to the combined action of Tb and Fe ions, which allowed for more effective charge transfer and storage. After repeated cycling, the nanomaterials showed good stability for all Tb concentrations, with barely noticeable fluctuations in peak current and potential. For practical applications in energy storage and conversion devices, where long-term performance is critical, this stability is required [40,41]. These nanoparticles improved electrochemical characteristics, especially at greater Tb concentrations, point to possible uses in a variety of industries. These include electrocatalysis, where effective redox activity can

enhance catalytic performance, and supercapacitors. Furthermore, the ability to control the electrochemical activity by altering the concentration of Tb provides a flexible framework for creating materials that are specifically suited for a range of uses.

4. Conclusion

In this work, we used a solvothermal technique to successfully manufacture Fe₃O₄:xTb (x = 0.25, 0.50, 0.75) nanomaterials. Using XRD, Raman spectroscopy, SEM, TEM, FTIR, and Cyclic Voltammetry (CV) investigations, a thorough characterisation was completed. The presence of Fe₃O₄ and Tb-doped Fe₃O₄ phases was shown by clearly defined diffraction peaks in the XRD findings, which verified the synthetic materials' crystalline character. The XRD data's determination of the crystallite sizes showed a steady and regulated growth of the nanoparticles, which is essential for their use in energy storage devices. The produced nanomaterials' phase purity and structural integrity were further validated by Raman spectroscopy, which also revealed distinctive vibrational modes. The morphological examination carried out with TEM and SEM revealed unique morphological features impacted by Tb doping and a uniform distribution of nanoparticles. Enhancing electrochemical performance and maximizing surface area require certain morphological features. The effective integration of Tb ions into the Fe₃O₄ matrix was confirmed by FTIR analysis, which also shed light on the functional groups that were present on the surface of the nanoparticles. These materials are good candidates for energy conversion and storage applications because of their remarkable specific capacitance and charge-discharge stability, which were found by cyclic voltammetry investigation. These qualities make them attractive candidates for energy conversion and storage applications in the future, which could lead to improvements in sustainable energy technology.

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