

Optical Property Enhancement in Cobalt Doped Magnetite Nanoparticles Evaluated with UV Vis Tauc and Urbach

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ABSTRACT

Magnetite (Fe_3O_4) is a spinel-based material that has broad potential in various applications, one of which is for magneto-optics. However, the value of the energy gap obtained from magnetite is too small to be applied. Efforts to improve these characteristics are carried out through transition metal ion doping techniques, one of which is cobalt (Co^{2+}) which is known to modify the electronic structure and stabilize the crystal lattice. This study aims to analyze the optical properties of magnetite nanoparticles that have been doped with Co^{2+} through energy gap and Urbach energy calculations. The synthesis of $\text{Co}_{0.125}\text{Fe}_{2.875}\text{O}_4$ was carried out using the coprecipitation method. Furthermore, characterization was carried out using UV-Vis spectroscopy and analyzed the size of the energy gap and Urbach energy. The results showed that cobalt doping ($\text{Co}_{0.125}\text{Fe}_{2.875}\text{O}_4$) produced two indirect energy gap values of 2.07 eV and 3.19 eV and one direct energy gap value of 3.63 eV. Urbach energy analysis revealed a very low E_u value of 0.0073 eV, indicating high crystal regularity and minimal structural defects in the material. This study demonstrated that cobalt doping not only increases the band gap energy of magnetite but also significantly lowers the Urbach energy, resulting in a material with more pronounced optical properties.

Keywords: Magnetite, Doping, Cobalt, Energy gap, Urbach Energy

1. INTRODUCTION

Magnetite (Fe_3O_4) is a metal oxide-based material with an inverse spinel structure, where Fe^{3+} ions occupy both tetrahedral (A) and octahedral (B) sites, while Fe^{2+} ions are distributed in octahedral sites [1]. This unique structure provides distinctive magnetic properties and enables its application in various fields such as data storage, magnetic sensors, contrast agents in magnetic resonance imaging (MRI), and magnetic field-based drug delivery systems [2]. In addition to its magnetic properties, magnetite also possesses optical properties relevant for applications in photocatalysis, optoelectronics, and magneto-optical devices. However, pure magnetite has significant limitations in its optical properties, with a relatively narrow band gap (around 2.0–2.2 eV) and a high level of structural defects, resulting in the formation of tail states within the energy gap [3]. In Fe_3O_4 , the predominant structural defects include non-stoichiometry ($\text{Fe}_{3-\delta}\text{O}_4$) that generates cation vacancies, Fe interstitials, and oxygen vacancies; these perturb the $\text{Fe}^{2+}/\text{Fe}^{3+}$ ratio and introduce localized states within the band gap [4]. Additionally, antiphase boundaries in the inverse spinel lattice, together with grain boundaries and nanoparticle surfaces, disrupt Fe–O–Fe pathways, increase scattering, and enrich tail states. Charge and orbital disorder associated with the Verwey phenomenon, which remains only partially ordered at room temperature, further broadens the optical absorption edge [5]. Optically, the accumulation of these defects manifests as a wider Urbach energy and an increased Urbach energy (E_u). This condition can reduce the efficiency of electron transitions and limit the material's performance in optical-based applications [6], [7]. The improvement of magnetite's performance has been extensively pursued through nanostructure engineering and transition metal ion doping. Among the various dopants used, cobalt (Co^{2+}) is an attractive candidate due to its unique electronic properties. Cobalt has an electron configuration of $[\text{Ar}] 3d^7$, which allows strong interactions with oxygen atoms in the spinel lattice, thereby modifying super-exchange interactions between metal cations [8]. Several studies have reported that Co^{2+} substitution at octahedral $\text{Fe}^{2+}/\text{Fe}^{3+}$ sites can increase magnetic anisotropy, strengthen metal-oxygen bonds, and affect the energy band structure [8], [9]. Thus, cobalt doping is believed to widen the band gap energy of magnetite while increasing structural order by reducing the level of crystal defects.

Although cobalt doping in magnetite has been widely reported, most studies emphasize magnetic properties. Systematic investigations connecting cobalt doping to optical behavior, specifically through band-gap and Urbach-energy (E_u) analyses

remain limited. This gap motivates the present study [10]. Urbach energy is a quantitative indicator of lattice disorder that governs sub-gap absorption and band-edge sharpness in ferrites [11]. A low E_u value indicates a material with good crystal order and a minimum of electron trap states, which is essential for efficient optical and electronic applications. The lack of studies integrating band gap and Urbach energy analysis simultaneously represents a research gap that needs to be filled. Furthermore, there is an urgent need to understand how cobalt doping directly affects the electronic structure of magnetite. The substitution of Co^{2+} cations, which differ in ionic size and electron configuration from Fe^{2+} , is believed to create local distortions in the spinel lattice, which can modify the separation of the valence band ($\text{O}2p$) and conduction band ($\text{Fe}3d$). This mechanism, if not fully understood, will limit the optimization of material synthesis for advanced technological applications [12]. Prior studies on cobalt-doped magnetite have largely reported optical band gaps, while quantitative E_u analyses are scarce. As a consequence, material selection often relies on band-edge positions alone and overlooks disorder-driven sub-gap absorption. Establishing E_u alongside direct/indirect band gaps provides a practical screening metric for tail-state density and band-edge sharpness—parameters that directly govern optical loss and device stability.

Functional-material technologies increasingly demand compounds with stable spectra and minimal optical losses. In optoelectronics, wide band gaps and high crystal regularity help maintain spectral stability and limit recombination-driven energy loss [3]. In photocatalysis, a larger band gap permits more effective use of high-energy photons, while a lower E_u suppresses defect centers that act as electron–hole recombination sites. Within this context, tailoring magnetite through cobalt incorporation offers a direct route to adjust the electronic structure and sharpen the absorption edge, extending its practicality for advanced devices. Prior reports point in this direction [11], [13]. CoFe_2O_4 nanoparticles exhibit band-gap widening to 3.3–3.6 eV with an accompanying reduction of E_u to ~0.01 eV, consistent with improved crystal quality. Additional studies show that Co^{2+} strengthens Co–O bonding in the spinel lattice, thereby reducing disorder and defect density [14]. Yet most investigations have treated band-gap and Urbach metrics separately, making it difficult to relate edge positions to tail-state density in a single, comparable framework. Here, UV–Vis spectroscopy is employed to extract direct and indirect band gaps alongside E_u from the same dataset via Tauc and Urbach analyses, allowing band-edge evolution to be read in concert with sub-gap tail behavior. This integrated optical assessment clarifies how cobalt modifies magnetite’s electronic structure and provides concise, defect-sensitive criteria for material selection in optics-driven applications.

Based on this background and existing research gaps, this study focuses on analyzing the modification of the optical and structural properties of magnetite nanoparticles through cobalt doping, with an emphasis on calculating the band gap energies (direct and indirect band gaps) and Urbach energy as indicators of crystal order.

2. METHOD

The materials used in this study include natural iron sand (Loang Balok Beach, Mataram) as the main source of iron (Fe) ions, hydrochloric acid (HCl 38%, Merck German), ammonium hydroxide (NH_4OH 25%, Merck German), cobalt chloride hexahydrate ($\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$), and distilled water as solvents. The equipment used includes a magnetic stirrer, filter paper, and a UV-Vis spectrophotometer (LW Scientific V-200-RS Spectrophotometer, USA) for optical characterization. A total of 20 grams of iron sand was dissolved in 58 mL of 38% HCl and stirred using a magnetic stirrer at a speed of 300 rpm until a homogeneous solution was formed. The solution was then filtered to separate the insoluble solid residue. A total of 15 mL of the filtered $\text{FeCl}_2 \cdot \text{FeCl}_3$ solution was added with 5.06 grams of $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ according to stoichiometric calculations. Nanoparticle precipitation was carried out by gradually adding 25 mL of NH_4OH solution (25%) while stirring until cobalt ferrite (CoFe_2O_4) precipitate was formed [8]. The precipitate was then washed repeatedly using distilled water until it reached a neutral pH. The neutralized product was then dried through a calcination process at 100 °C for 60 minutes, then ground into a fine powder. All syntheses used the procedure from A. G. Leonel et al, which produced magnetite nanoparticle material using the coprecipitation method, so it is appropriate for use in this study [8]. Optical characterization was carried out using a UV-Vis spectrophotometer to obtain an absorption spectrum in the wavelength range of 200–800 nm. The absorption spectrum data were used to calculate the band gap energy value using the Tauc Curve method, both for direct and indirect allowed transitions, according to the equation [13]:

$$(\alpha h\nu)^n = A(h\nu - E_g) \quad (1)$$

where α is the absorbance coefficient, $h\nu$ is the photon energy, A is the material constant, and n is an index indicating the type of optical transition ($n = 1/2$ for direct transitions and $n = 2$ for indirect transitions). The band gap energy is obtained by extrapolating the linear curve $(\alpha h\nu)^n$ against the photon energy until it intersects the energy axis. In addition, the Urbach energy (E_u) is calculated from the exponential tail of the absorbance spectrum using the relationship [14]:

$$\alpha = \alpha_0 \exp\left(\frac{h\nu}{E_u}\right) \quad (2)$$

by plotting $\ln a$ against $h\nu$ and determining E_u from the inverse of the gradient of the straight line. The selection of the UV-Vis method in this study is based on its relevance to identify the optical properties of materials, especially in determining the band gap energy value that reflects the electron transition between bands and the regularity of the crystal structure indicated by the Urbach energy.

3. RESULTS AND DISCUSSION

Initial analysis of the optical properties of cobalt-doped magnetite nanoparticles was performed using UV-Vis spectroscopy to observe light absorption patterns at specific wavelengths. This characterization aims to evaluate the effect of cobalt doping on the optical behavior of the material, particularly in relation to the electron transition from the valence band to the conduction band [14]. The UV-Vis spectrum reveals the characteristic absorption peak of metal-oxygen (Fe-O) bonds in the spinel magnetite lattice at 509.26 nm. It also captures shifts in peak position arising from the substitution of Co^{2+} ions [15]. Observations of this absorption spectrum provide an important basis for understanding how cobalt doping modifies electronic interactions in magnetite. Shifts in the absorption peak position and changes in absorbance intensity can reflect the formation of intermediate states, increased band separation, or altered metal-oxygen bond regularity, with an energy change of 0.84%. The results of the UV-Vis characterization are presented in Figure 1.

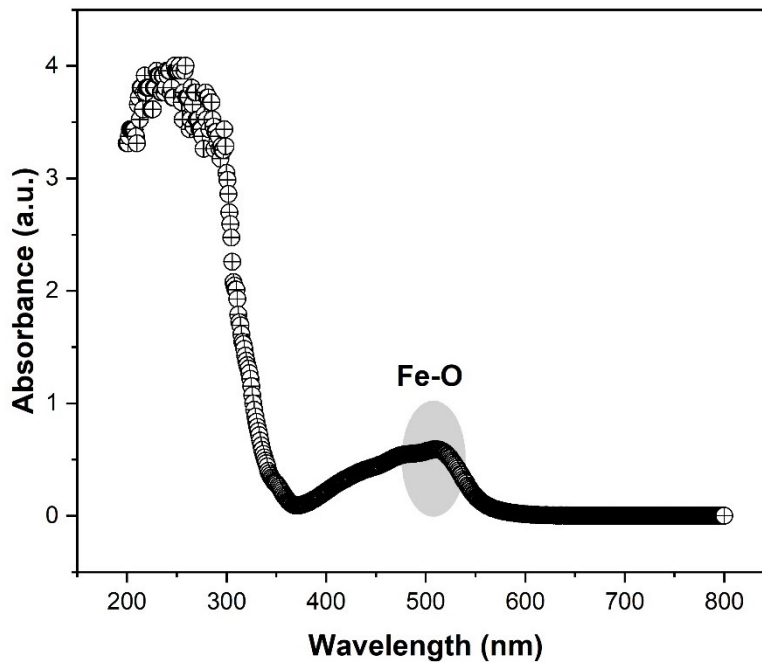


Figure 1. Graph of Absorbance Value of Cobalt-doped Magnetite

UV-Vis analysis of cobalt-doped magnetite samples reveals a typical absorbance pattern of metal oxide-based materials with a spinel structure. A high absorbance peak is observed in the ultraviolet range (200–300 nm), indicating a band-to-band transition between the valence band and the conduction band (Fe-O) electron transition within the magnetite structure. A significant decrease in absorbance in the 350–450 nm region indicates the characteristics of a semiconductor with a distinct optical energy gap [8]. Furthermore, a weak absorption peak is observed around 500–550 nm, associated with the d-d transition of Co^{2+} and Fe^{3+} ions or Fe-O charge transfer, which occurs due to cobalt doping [16]. This phenomenon indicates that the addition of Co^{2+} ions has modified the electronic structure of magnetite and potentially improves the material's optical properties.

These results are consistent with previous studies that reported that cobalt doping in magnetite causes a blue shift in the absorption edge toward shorter wavelengths and an increase in the band gap energy value. For example, studies on Co-doped ferrite nanoparticles show that the band gap increases from around 1.5 eV in pure magnetite to up to 2.6 eV after Co doping, as new energy levels are formed in the spinel structure [17]. Other studies also report a main absorbance peak in the ultraviolet region (380–400 nm) associated with the Fe-O transition, as well as an additional peak around 490–520 nm associated with the d-d transition of Co^{2+} ions [18]. The difference in peak position between the results of this study and the literature is likely due to the smaller particle size, which gives rise to quantum confinement effects, which generally shift the absorption edge to shorter wavelengths.

Next, an energy gap (E_g) analysis was performed using two equations, the direct energy gap and the indirect energy gap, the results of which are shown in Figure 2.

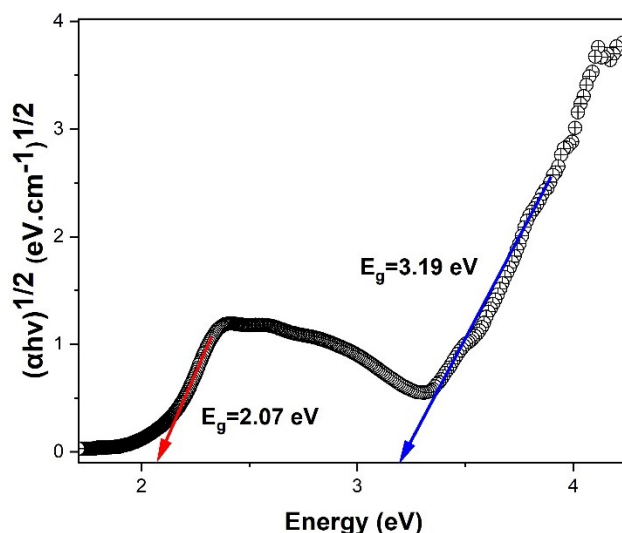


Figure 2. Graph of In-Direct Calculation of Band Gap Energy of Cobalt Doped Magnetite Nanoparticles using Tauc Curve Method

Figure 2 shows a graph of the indirect band gap energy calculation of cobalt-doped magnetite nanoparticles using the Tauc Curve method. From the analysis results, two band gap energy values were obtained, namely $E_g = 2.07 \text{ eV}$ and $E_g = 3.19 \text{ eV}$. This double band gap energy value indicates the existence of two optical transition mechanisms that occur in the material. The lower band gap energy ($E_g = 2.07 \text{ eV}$) is associated with an indirect allowed transition originating from the defect states or the influence of surface functional groups formed due to cobalt doping. Meanwhile, the higher band gap energy ($E_g = 3.19 \text{ eV}$) is associated with a direct transition that occurs in the crystalline core structure of magnetite. The phenomenon of the emergence of two band gap energy values was also reported in previous studies of magnetite nanoparticles and transition metal-doped ferrite-based materials, where metal doping can modify the electronic structure by creating additional energy levels within the band gap (mid-gap states), thus enabling multiple optical transitions [19].

Materialistically, the substitution of Co^{2+} ions, which have ionic radii and electron configurations different from those of Fe^{2+} , causes local distortions in the magnetite crystal lattice. These distortions alter the super-exchange interactions between metal ions ($\text{Fe}^{2+}/\text{Fe}^{3+}$) via oxygen atoms, ultimately modifying the material's electronic band structure. Similar results have been reported in studies of cobalt-doped ferrite, where the addition of Co^{2+} increases local potential heterogeneities and generates local energy levels that facilitate additional optical transitions [20].

Furthermore, direct energy gap calculations are shown in Figure 3.

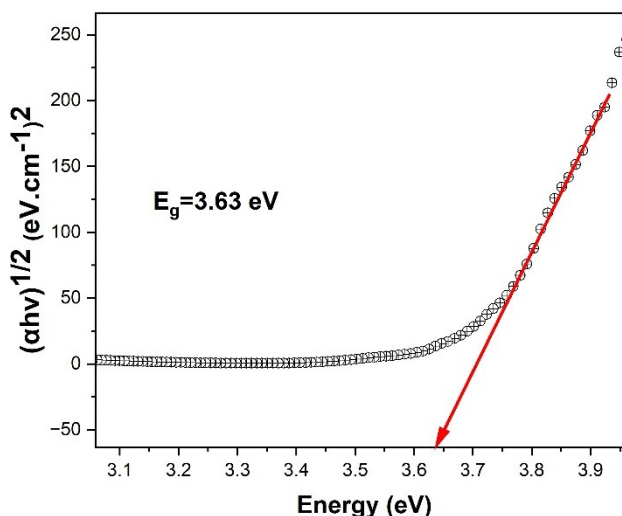


Figure 3. Graph of direct calculation of band gap energy of Cobalt Doped Magnetite Nanoparticles using Tauc Curve Method

Figure 3 further shows the direct band gap energy calculation for the same sample, where the value of $E_g = 3.63 \text{ eV}$ is obtained, higher than the intrinsic band gap value of magnetite which is generally in the range of 2.0–2.2 eV. This high value can be explained by the influence of cobalt doping which replaces Fe^{2+} ions on octahedral sites, thereby changing the electron configuration in the spinel lattice. The substitution of Co^{2+} ($3d^7$), ions which have a different electron configuration from Fe^{2+} ($3d^6$) affects the separation of energy bands (band splitting) between the conduction band (Fe 3d) and the valence band (O 2p) through the Co–O–Fe super-exchange interaction. This change increases the energy required for the direct transition of electrons from the valence band to the conduction band.

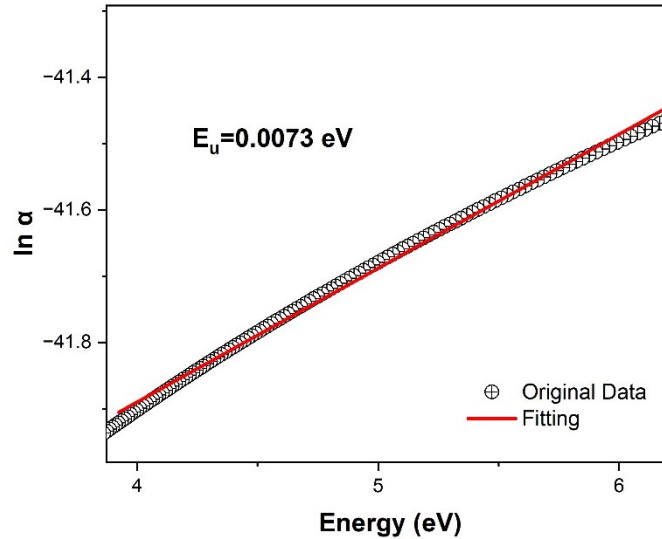


Figure 4. Urbach Energy Value Graph for Cobalt-doped Magnetite

Co^{2+} doping in magnetite directly influences the material's band structure by modifying local orbital interactions and shifting the energy levels of transition metal ions. Co^{2+} has a different electron configuration ($[\text{Ar}] 3d^7$) compared to Fe^{2+} ($[\text{Ar}] 3d^6$), and when it substitutes Fe^{2+} in the octahedral sites, it redistributes the electronic density near the valence and conduction bands [21]. More specifically, Co^{2+} ions generate a stronger octahedral crystal field, which increases the energy separation between d orbitals and reduces the density of low-energy states that are involved in optical transitions [20], [22]. This results in higher energy requirements for electronic excitation and manifests as a widened band gap and a blue shift in the absorption edge. This behavior is supported by findings where the band gap increased from 2.10 eV to 2.55 eV with increasing cobalt concentration in magnetite nanoparticles [23].

The band gap enlargement observed ($>3 \text{ eV}$ in this study) suggests that optical transitions are more discrete due to reduced overlap of Fe^{2+} states in the conduction band, supporting the conclusion that cobalt modifies the band structure significantly. The E_u , evaluated from the absorption spectrum, is found to be as low as 0.0073 eV. This remarkably low value indicates minimal tail states, which are typically caused by localized energy variations near the band edges. The reduction in E_u is not merely due to improved structural order but can also be attributed to a more homogeneous local electronic environment induced by cobalt doping. Cobalt, due to its stronger and more directional bonding nature, stabilizes the local potential around its lattice site, thereby reducing fluctuations that usually lead to the formation of sub-bandgap states. These observations are consistent with results from cobalt-doped magnetite nanoparticles, where doping reduced electronic disorder and improved optical clarity [22]. Additionally, similar results were reported in Ni- and Co-doped iron oxide systems, where the band gap increased and the optical absorption became more defined as the Co^{2+} content increased [24], [25]. These trends confirm that cobalt doping improves the sharpness of optical transitions by limiting localized defect states and enhancing electronic uniformity.

Furthermore, the low Urbach energy has important implications for materials technology applications. Optically, low E_u means fewer local energy levels within the energy gap that can act as trap states. This is advantageous for optoelectronic applications because it allows for more efficient electron transitions without energy loss due to trapping. Furthermore, in the context of photocatalysis or oxide semiconductor-based sensors, materials with low E_u tend to have lower charge carrier recombination, thus enhancing their functional activity. Compared with other literature on pure magnetite, which typically has E_u in the range of 0.02–0.05 eV, the significantly lower E_u value in this study reflects the positive effect of cobalt doping on improving structural quality and reducing defect levels. In other words, in addition to increasing the band gap energy (as seen in Figure 2 and Figure 3), cobalt doping also significantly lowers the Urbach energy, resulting in a unique combination of a high band gap and minimal optical defect levels.

4. CONCLUSION

This study has successfully analyzed the optical properties of cobalt-doped magnetite nanoparticles through UV-Vis spectroscopic characterization, band gap energy calculation using the Tauc Curve method, and Urbach energy analysis. The results obtained indicate the presence of two indirect band gap values of 2.07 eV and 3.19 eV, respectively, and one direct band gap value of 3.63 eV. A very low Urbach energy of 0.0073 eV indicates high crystal regularity, minimal disorder at the band edge, and a more homogeneous cation-oxygen framework after doping. This condition confirms that the presence of Co^{2+} ions not only plays a role in modifying the electronic properties, but also improves the overall structural quality of magnetite. These results are consistent with previous studies on cobalt-doped ferrite, which reported an increase in the band gap value, a shift in the absorption edge to shorter wavelengths (blue shift), and a decrease in the Urbach energy due to increased crystallinity and stability of the spinel structure.

5. ACKNOWLEDGEMENT

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