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# Substituted effect of Al<sup>3+</sup> on structural, optical, magnetic and photocatalytic activity of Ni ferrites

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## Abstract

Al-substituted nickel ferrite NiAl<sub>x</sub>Fe<sub>2-x</sub>O<sub>4</sub>, where x = (0.00, 0.05, 0.10 and 0.15) synthesized through chemical co-precipitation method were investigated for their structural, morphological, optical and magnetic characterization. Al<sup>3+</sup> substitution plays a significant role in the properties of the ferrite nanoparticles. The TGA showed three mass losses, whereas DTA resulted in three endothermic peaks. Rietveld refined XRD revealed the development of single phase cubic spinel with crystallite sizes around 28 - 36 nm for aluminum substituted samples. TEM and SEM analysis showed the monodispersion and cubic-like nanostructure. The room temperature infra-red spectra showed the features of higher and lower energy bands detected at  $\nu_1 \sim 589\text{-}595\text{ cm}^{-1}$  and  $\nu_2 \sim 405\text{-}409\text{ cm}^{-1}$ , respectively corresponded to octahedral vibration (O-band) and tetrahedral (T-band) complexes that also verify the creation of spinels ferrites. The Raman spectra showed five Raman active modes ( $A_{1g} + E_g + 3T_{2g}$ ) which are estimated in the spinel structure. The optical study showed that the compounds have an

optical band gap between 1.60 and 1.89 eV. Mössbauer spectra elucidate the nature of the phases and cation distribution. From the hysteresis loop, it is clear that the synthesized samples can be control, for the  $\text{NiAl}_x\text{Fe}_{2-x}\text{O}_4$  nanoferrites. The photocatalytic activity of Al-substituted nickel ferrite were studied based on the degradation of methyl orange as a model compound, where the results showed that  $\text{NiAl}_{0.15}\text{Fe}_{1.85}\text{O}_4$  a good photocatalytic activity.

## **Keywords:**

Spinel ferrites ( $\text{NiAl}_x\text{Fe}_{2-x}\text{O}_4$ ); Co-precipitation; Substitution; Magnetic parameters; Photocatalysis.

## **1. Introduction**

For half a century, nanotechnologies have covered a large number of technological fields whose common denominator is the nanometric size of structures. This is a major theme of research for both basic science and applications, relying heavily on the development of nanomaterials [1-3]. Spinel ferrites ( $\text{MFe}_2\text{O}_4$ ) are one of the most important classes of magnetic materials. They already have many fields of application, because of their original magnetic properties, their low cost of production, compared to better known magnetic materials based on precious metals [4-6]. The most common applications are magnetic recording, and use as a massive component for power and permeability applications [7-12]. Spinel is a generic term for a crystalline structure of the general formula  $\text{A}^{2+}\text{B}_2^{3+}\text{O}_4$  (A and B representing metal cations) [13, 14]. The crystallographic structure adopts the space group belonging to the cubic system, Fd-3m (No. 227 in the international tables) with a mesh parameter of the order of 8.4 Å. This structure is constructed from the cubic compact arrangement of oxygen ions within which the actions are distributed among the tetrahedral sites (Th) which will be designated by the notation A, and the octahedral sites (Oh) which will be these cubic faces-centered cubicles defined by the oxygens contain 32 octahedral sites, 16

of which are occupied, and 64 tetrahedral sites, 8 of which are occupied. To describe the structure, divide the parameter mesh into 8 cubes called an octant of edge  $a / 2$ . The magnetism of spinel nanoferrites is derived from super exchange between cations in tetrahedral (A-site) and octahedral (B-site) including A–B exchange, B–B exchange and A–A exchange. Therefore, the magnetic parameters of spinel are associated to the distribution species of cations in A-site and B-site. The properties of spinel ferrites are influenced by method used for the synthesis, chemical composition and cation distribution [15, 16]. Many methods have been developed to prepare nanocrystallite  $AB_2O_4$  namely organic gel-thermal decomposition method, sol–gel auto-combustion method, co-precipitation method, gel-assistant hydrothermal route, hydrothermal method, thermolysis, citric acid combustion method, self-propagating, wet chemical coprecipitation technique, microemulsion and polymer assisted coprecipitation method [17–30]. Chemical co-precipitation method is mostly attractive thanks to its low cost, short preparation time, high homogeneity and purity, relatively low reaction temperature and well-crystallized product.

Al-substituted Ni ferrites have specific properties with respect to ferrite nickel, for example: the addition of Al inhibits particle growth and improves the mechanical strength of ferrites [31]. In addition, the addition of  $Al^{3+}$  increases the resistivity and thus decreases the dielectric losses, and also decreases the saturation magnetization. In addition, the addition of  $Al^{3+}$  reduces magnetic coercivity and causes ferrite to become softer for some high frequency applications.

In this work we investigate the effect of aluminum (Al) substitution on the structural, morphological and magnetic properties of prepared by co-precipitation method. We have used co-precipitation method which stands for a simple procedure to synthesize spinel ferrites nanoparticles. The synthesized compounds are well characterized for their structural, morphological, optical and magnetic properties by various characterization techniques such as

Thermo Gravimetric Analysis (TGA), Differential Thermal Analysis (DTA), X-ray diffraction (XRD) with Rietveld refinement technique, Transmission Electron Microscopy (TEM), Scanning Electron Microscopy (SEM), Fourier Transform Infra-Red (FT-IR) spectroscopy, Raman spectroscopy, Ultraviolet-Visible (UV-Vis) analysis, Mössbauer spectroscopy and Vibrating Sample Magnetometer (VSM).

## 2. Experimental

### 2.1. Materials

Chemicals with high purity were purchased from Aldrich and used without further purification. Deionized distilled water was used for all the experiments. The raw materials are: (FeCl<sub>3</sub>, 6H<sub>2</sub>O), (NiCl<sub>2</sub>, 6H<sub>2</sub>O), (AlCl<sub>3</sub>, 6H<sub>2</sub>O), (NaOH), acid oleic (C<sub>18</sub>H<sub>34</sub>O<sub>2</sub>) and ethanol (C<sub>2</sub>H<sub>6</sub>O).

### 2.2. Synthesis of NiAl<sub>x</sub>Fe<sub>2-x</sub>O<sub>4</sub> nanoparticles

Nanosized (NiAl<sub>x</sub>Fe<sub>2-x</sub>O<sub>4</sub>), where x = (0, 0.05, 0.10, 0.15) particles were synthesized by facile co-precipitation method. The starting materials nickel chloride hexahydrate (NiCl<sub>2</sub>,6H<sub>2</sub>O), aluminum chloride hexahydrate (AlCl<sub>3</sub>,6H<sub>2</sub>O) and iron chloride hexahydrate (FeCl<sub>3</sub>,6H<sub>2</sub>O) were weighed in a well determined stoichiometric ratio, and dissolved separately for 15 minutes in order to have an apparent and homogeneous solution. Then, 3M of the mineralizer, NaOH was added in the admixing solution in order to maintain pH 11 and a few drops of oleic acid as a surfactant and coating material [32]. The solution was maintained at an ambient temperature of 80°C for 3 hours to obtain brown precipitate. The precipitate thus obtained was magnetically separated by washing several times with deionized distilled water and ethanol and the byproduct was dried overnight at 80 °C under air atmosphere in an oven. Then the dried powder was ground well and sintered at the temperature 700 °C for 6 h in a furnace.

### **2.3. Characterization**

The thermal behavior was evaluated by Thermo Gravimetric (TGA) and Differential Thermal Analysis (DTA) in the air with TGA Q500 TA instrument. The X-ray diffraction patterns of the compounds were identified by German Bruker D2 PHASER X-ray diffractometer with  $\text{CuK}\alpha$  radiation (1.5418 Å) as a source. The intensity data were collected over the range of 20°–80° using a step scan mode (0.001°/s). The data were processed to analyze all of the samples using the computer Program FullProf.2k (Version 4.30—Apr 2008-ILL JRC) in the Rietveld method for structure refinement. The TEM micrographs were obtained on a JEOL 2011 transmission electron microscope with an accelerating voltage of 200 kV. Micro structural characteristics such as morphology and particle size of compounds were analyzed through scanning electron microscope (SEM) with KYKY-EM3200, 25KV type. Fourier Transform Infra-Red (FT-IR) spectra of samples were explored through a NICOLET IR200 FT-IR spectrometer with transmission from 4000 to 400  $\text{cm}^{-1}$ . The Raman spectra were composed using a Renshaw in Via Raman microscope with a 50x objective coupled to a 632.80 nm He-Ne laser excitation source (Renshaw RL633). The Ultraviolet-Visible (UV-Vis) absorption of the compounds was recorded on SHIMADZU (UV-3101 PC) UV-Vis Spectrophotometer. The  $^{57}\text{Fe}$  Mössbauer spectra were collected on a FAST Comtec Mössbauer system at room temperature, using a  $^{57}\text{Co}$  (Pd) source and a conventional constant acceleration mode. Magnetization measurements were performed by the vibrating sample magnetometer (VSM).

### **2.4. Photocatalytic activity measurements**

The photocatalytic activities of the  $\text{NiAl}_x\text{Fe}_{2-x}\text{O}_4$  nanoparticles with  $x = (0.00, 0.05, 0.10, \text{ and } 0.15)$  were analyzed based on the photodegradation of MO at room temperature. The solution was irradiated with visible medium pressure xenon lamp (150 W) under magnetic stirring. In a typical photocatalytic experiment, 0.1 g of the sample was dispersed in

100 mL of MO aqueous solution. Before applying the irradiation, the suspension was magnetically stirred for 30 min in the dark to ensure that an adsorption–desorption equilibrium was reached between the  $\text{NiAl}_x\text{Fe}_{2-x}\text{O}_4$  nanoparticles and the aqueous dye solution. Samples of the solution were then collected from the reactor at regular intervals, before centrifuging and analyzing to determine the residual amounts of the dye after photo-irradiation using a UV-Vis spectrophotometer (Shimadzu UV-2450).

### 3. Results and discussion

#### 3.1. Thermal behavior and phase analysis

The findings associated with formation and decomposition phase occurring during heat treatment of synthesized samples ( $\text{NiAl}_{0.05}\text{Fe}_{1.95}\text{O}_4$ ) are in excellent agreement through Thermo Gravimetric Analysis and Differential Thermal Analysis (TGA and DTA) results. Thermal analyses were carried out from 37 to 700 °C. TGA of the synthesized compound was performed by heating the samples in air atmosphere at 10 °C/min. **Fig. 1** depicts the thermal analyses (TGA, DTA) for spinel ferrite ( $\text{NiAl}_{0.05}\text{Fe}_{1.95}\text{O}_4$ ).

**Fig. 1** shows there were three distinct mass losses: the first was 5.56 % and occurred gradually between [44 °C – 182 °C]. This is attributed to the removal of water existing on the surface of prepared compound. One endothermic peak at 99.82 °C was observed using DTA. The second mass loss of 3.04 % occurred at [182 °C – 540 °C], which is due to the combustible organic products (acid oleic ( $\text{C}_{18}\text{H}_{34}\text{O}_2$ )) present in our prepared sample. Through the use of DTA we recorded one endothermic peak at 186.28 °C. The third mass loss stands for a minor weight loss (1.38 %) occurring in the range of [540 °C – 650 °C], which is due to the transition phase of prepared samples. Furthermore, using DTA helped us find one endothermic peak in DTA at 656.02 °C. As can be seen from this figure, after 660 °C the curve becomes parallel with the temperature axis which emphasizes the high stability of

NiAl<sub>0.05</sub>Fe<sub>1.95</sub>O<sub>4</sub> nanoparticles. There is no associated signal with the thermal processes of spinel ferrite nanoparticles in the TGA curve confirming their crystallization and phase transition.

### 3.2. X-ray diffraction analysis

Rietveld refined XRD patterns of NiAl<sub>x</sub>Fe<sub>2-x</sub>O<sub>4</sub> (x = 0.00, 0.05, 0.10 and 0.15) are presented in **Fig. 2**. The formation of single phase cubic spinel structure similar to that of ICDD card (No. 86-2267) with space group Fd-3m was revealed by XRD patterns. The characteristic diffraction peaks of cubic structure as well as the crystal structure, both are maintained throughout aluminum substitution without any noticeable impurity peak [33, 34].

The analysis of XRD patterns reveals the nanocrystalline nature of the prepared samples. The average crystallite size,  $D_{XRD}$ , for each sample was estimated from the most intense peak (311) using Scherrer's formula [35-38].

$$D_{XRD} = \frac{k \lambda}{\beta \cos \theta} \quad [1]$$

Where  $k$  is the so-called shape factor (0.9),  $\lambda$  is the wavelength (0.15418 nm, CuK $\alpha$ ),  $\beta$  is the full width at half maximum (FWHM), and  $\theta$  is the diffraction angle. The average crystallite size was found to decrease from 36 nm to 28 nm with increasing Al<sup>3+</sup> substituted. The XRD data were processed for Rietveld refinement of structure by FullProf.2k program. **Table 1** lists the Rietveld refinement parameters, crystallite size, and degree of crystallinity. The quality of the refinement was quantified by the corresponding figures of merit: profile residual  $R_p$ , weighted profile residual  $R_{wp}$  and goodness of fit  $\chi^2$  [39].

The lattice constant calculated by the Rietveld method and the values are listed in **Table 1** and was found to decrease from 8.280 to 8.223 Å with the increase in aluminum



concentration, which suggested the formation of a compositionally homogeneous solid solution and was found to be within the range of the lattice constants of  $\text{NiFe}_2\text{O}_4$ . **Fig. 3a** clearly showed the continuous shift in  $2\theta$  with increasing Al concentration. It is also clear from **Fig. 3a** that the angle shifts towards higher values. This shift is attributed to decrease in lattice parameter.

The decrease in the lattice parameter with  $\text{Al}^{3+}$  ion substitution which is ascribed to the ionic radius difference between the substituted  $\text{Al}^{3+}$  (0.051 nm) and the displaced  $\text{Fe}^{3+}$  (0.064 nm) ions which is in accordance with Vegard's law [40]. The variation of lattice constant with  $\text{Al}^{3+}$  substitution inevitably supports the occupancy of the Al ions into the host Ni ferrite lattice. The variation of average crystallite size ' $D_{\text{XRD}}$ ' and lattice parameter 'a' with the Al concentration is given in **Fig. 3b**.

### ***3.3. Particle size and morphology measurements: TEM, SEM***

The morphology of prepared ferrite nanopowders was determined through transmission electron microscope. Representative micrographs showing the surface morphology of  $\text{NiAl}_x\text{Fe}_{2-x}\text{O}_4$  ferrites with different Al-content are demonstrated in **Fig. 4a**. TEM studies indicated that the average particle size of Ni-Al ferrites decreases with the increase of  $\text{Al}^{3+}$  content. This leads to the fact that, as the  $\text{Fe}^{3+}$  ions are substituted by  $\text{Al}^{3+}$  ions, the potential changes in lattice parameter leads to the lattice strains. Consequently, internal stress is developed onto the ferrites compounds that hinders the particle growths. Thus, the particle sizes of the Al-substituted Ni ferrites are reduced [41].

**Fig. 4b** shows morphological pattern of the synthesized ferrites powder taken via scanning electron microscope. SEM images of  $\text{NiAl}_x\text{Fe}_{2-x}\text{O}_4$  showed the crystalline nature of the prepared nanoparticles and provide such a type of agglomeration. Substitution effects on the structures and particles sizes were determined. The particle size and morphology of the

compounds seem to be uniform with somewhat agglomeration in the prepared samples which is unavoidable. **Fig. 4b** indicates cubic-shaped nanoparticles of  $\text{NiAl}_x\text{Fe}_{(2-x)}\text{O}_4$ . However, the mean crystalline size of the prepared ferrite was in the range of 28 – 37 nm. The size of nanoparticles decreased with the increased aluminum contents because the ionic radius of iron (0.64 Å) is higher than that of aluminum (0.51 Å).

### **3. 4. FT-IR spectra**

The FT-IR analysis also supports the formation of single phase.  $\text{NiAl}_x\text{Fe}_{2-x}\text{O}_4$ , where ( $x = 0.00, 0.05, 0.10, 0.15$ ) ferrite materials. **Fig. 5** shows FT-IR spectra of the Al substituted Ni nanoferrites in the frequency range of 400–800  $\text{cm}^{-1}$ . Two major absorption bands labeled as  $\nu_1$  and  $\nu_2$  correspond to the vibrations of the tetrahedral sites (A-O-A bonds) and the octahedral sites (B-O-B bonds), respectively [42-44]. The higher wavenumber band ( $\nu_1$ ) for all the samples, shifted from 589 to 595  $\text{cm}^{-1}$  and lower wavenumber ( $\nu_2$ ), shifted from 405 to 409  $\text{cm}^{-1}$  with the increased Al concentration. These bands confirmed the spinel structure of the prepared ferrite nanoparticles [45]. The observed shift in the peaks is expected and is due to modification in the occupation of the cations in tetrahedral (A) and octahedral (B) sites. It is well known that, the change in bond length has an inverse relation to the band frequency shift. Therefore, such increase in the frequency of absorption is due to the decrease in tetrahedral and octahedral bond lengths.

### **3 .5. Raman spectroscopy**

Raman spectra performed at room temperature in the frequency range of 200-900  $\text{cm}^{-1}$  of as synthesized  $\text{NiAl}_x\text{Fe}_{2-x}\text{O}_4$ , where ( $x = 0.00, 0.05, 0.10, 0.15$ ) ferrites samples are shown in **Fig.6**. These ferrites have cubic inverse spinel structure of type  $\text{AB}_2\text{O}_4$  belonging to Fd-3m (O7h) space group with eight formula units per unit cell. Although the full unit cell contains 56 atoms (8 molecules per unit cell), only 14 atoms are in the asymmetric unit and therefore

42 vibrational modes are expected. According to group theory, the irreducible representations for the studied systems are as follows:

$$\Gamma_{\text{irred}} = A_{1g}(\text{R}) + E_g(\text{R}) + T_{1g} + 3T_{2g}(\text{R}) + 2A_{2u} + 2E_u + 5T_{1u}(\text{IR}) + 2T_{2u} \quad [2]$$

The presence of an inversion center in the centro-symmetrical space group  $Fd3m$  implies mutual exclusion of Raman and IR activities for the same vibrational mode. There are five first-order Raman active modes  $A_{1g} + E_g + 3T_{2g}$  [46, 47] and all these modes were observed at ambient conditions whereas only the  $T_{1u}$  type normal vibrations modes are infrared-active.  $T_{1g}$ ,  $A_{2u}$ ,  $E_u$  and  $T_{2u}$  symmetry vibrations are the silent ones. All the IR-active vibrations are triply degenerated. A is for one dimensional representation, E for two and T for three dimensional representations, g denotes the symmetry with respect to the center of inversion.  $A_{1g}$  describes symmetric stretch of oxygen atoms along Fe–O (or M–O) tetrahedral bonds,  $T_{2g}(1)$ : translatory movement of the whole tetrahedron ( $\text{FeO}_4$ ),  $T_{2g}(2)$ : asymmetric stretch of Fe(M)–O bond,  $T_{2g}(3)$  and  $E_g$ : asymmetric and symmetric bends of oxygen with respect to Fe, respectively. In order to determine the natural frequency of the Raman active modes of each sample, a least square fit with Lorentzian line shape was used to fit the Raman spectra. The thick smooth lines are fits to the Lorentzian functions. The bands corresponding to these modes are observed at ambient conditions in Raman spectrum of  $\text{NiFe}_2\text{O}_4$  whose values are:

$$T_{2g}(1) = 213 \text{ cm}^{-1}, E_g = 337 \text{ cm}^{-1}, T_{2g}(2) = 488 \text{ cm}^{-1}, T_{2g}(3) = 574 \text{ cm}^{-1}, A_{1g} = 702 \text{ cm}^{-1}$$

These results are in good agreement with earlier reported data on  $\text{NiFe}_2\text{O}_4$  spinel [48-50].

### ***3.6. Diffuse reflectance spectroscopy (DRS) studies***

To study the effect of change in the concentration of substitution ( $\text{Al}^{3+}$ ) on the optical properties of aluminum doped  $\text{NiFe}_2\text{O}_4$  semiconductor ferrite materials, the UV–Visible

diffuse reflectance measurement was carried out. The band gap energy can be approximately calculated from the optical reflectance data by using the following equation [51-55]:

$$(\alpha h\nu)^n = A (h\nu - E_g) \quad [3]$$

Where  $\alpha$  is the absorption coefficient,  $A$  is constant,  $h\nu$  is the energy of light and  $n$  is a constant depending on the nature of the electron transition [56]. Spinel ferrites ( $MFe_2O_4$ ) has a direct band gap ( $n=2$ ) [57]. **Fig. 7a** shows the plot of  $(\alpha h\nu)^2$  versus  $h\nu$ . The energy gap can be obtained from the intercept of the linear absorption edge part with the energy axis. When  $(\alpha h\nu)^2$  is zero, the photon energy is  $E_g$ . The optical band gap of spinels ferrite was observed in **Table 2**. It is noted that the optical band gap increases with the increase in Al content (**Fig. 7b**).

### ***3.7. Mössbauer investigations***

The Mössbauer spectra recorded at 300 K for the samples  $x = 0.0, 0.05, 0.1$  and  $0.15$  are shown in **Fig. 8**. Mossbauer's parameters are collated in the **Table 3**. For  $x = 0.0-0.1$  the spectra exhibit a superposition of two Zeeman sextets (magnetic components) [58], one due to the  $Fe^{3+}$  ions at the tetrahedral (A) and the other due to  $Fe^{3+}$  ions at the octahedral (B) sites. The spectrum for  $x = 0.15$  was fitted the coexistence of magnetic as well as superparamagnetic components. The intensity of the central superparamagnetic doublet with respect to the magnetic sextets increases with increasing  $x$  values. Thus, as the content of non-magnetic  $Al^{3+}$  increases in  $NiAl_xFe_{2-x}O_4$  system, the magnetic coupling (ferrimagnetism) is weakened from that of Ni ferrites ( $x = 0$ ) to that of superparamagnetic composition ( $x = 1.0$ ).

### ***3.8. Magnetic properties***

The magnetization versus applied field for different samples is shown in **Fig. 9a**. The values of coercivity ( $H_c$ ), saturation magnetization ( $M_s$ ) and remanent ( $M_r$ ) of all the samples are extracted from these loops and tabuled in **Table 4**.

It is clear from **Fig. 9b** that the magnetization decreases with increasing Al content [59]. This effect can be explained by the following reasons.

Firstly, particle size: as the Al content increases the particle size decreases (**Fig.3b**). The existence of some degree of the spin canting in the whole volume of the nanoparticles and the disordered surface/dead layer at the surface can explain the decrease of the saturation magnetization.

Secondly, weakening of A–B interactions: as Al replaces some of the Fe ions, the magnetic coupling weakens because the Al ion itself does not carry the magnetic moment ( $1s^2 2s^2 2p^6$ ). The mechanism of the substitution can be described by replacing Ni cations with non-magnetic Al cations which prefer the octahedral sites. Then, it leads to the weakening of the A–B interactions and thus leads to a disturbance of the spin ordering, causing the destabilization of the magnetic ordering. In the spinel structure  $Ni^{2+}$  ions have a very strong preference for octahedral sites. Also,  $Fe^{3+}$  ions have a stronger preference for the tetrahedral sites as compared to the octahedral sites.

**Fig. 9b** exhibits the magnetic coercivity as a function of Al content. The reduction in magnetic coercivity with the Al content can be described as follows

a) Particle size. When the grain size reaches below the critical single domain size the magnetic coercivity decreases with the grain size ( $H_c \propto D^6$ ).

b) Magneto crystalline anisotropy. In addition to the Ni ( $[Ar] 4s^0 3d^8$ ) migration, another reason is the angular momentum of the Al ion.  $Al^{3+}$  has a zero angular momentum ( $l=0$ ) and does not contribute to magneto-crystalline anisotropy. As the Al ion ( $l=0$ ) replaces some of the Ni ions ( $d^8, l \neq 0$ ), the spin–orbit coupling weakens because  $Al^{3+}$  itself does not carry the angular momentum; consequently, the magnetic anisotropy and magnetic coercivity will decrease.

### 3.8. Photocatalytic Experiments

Photocatalytic experiments were carried out in the presence of the as-prepared (NiAl<sub>x</sub>Fe<sub>2-x</sub>O<sub>4</sub>) with (x = 0.00, 0.05, 0.10, 0.15) nanostructures as photocatalyst and methyl orange dye as organic pollutants under visible irradiation (Fig. 10a). The dye degradation percent was calculated as follows [60]:

$$\text{Percentage of degradation} = (1 - A_t / A_0) * 100 \quad [4]$$

Where A<sub>0</sub> and A<sub>t</sub> are the absorbance value of the solution at 0 and t min, respectively.

Blank experiments under Visible illumination without the nanoparticles were first bearded out to rationalize the photocatalytic activity of the (NiAl<sub>x</sub>Fe<sub>2-x</sub>O<sub>4</sub>) nanoparticles. This, blank experiment result Indicated that MO could not be decomposed without the photocatalyst. By contrast introduction of the photocatalysts induced the rapid degradation of MO. (NiAl<sub>x</sub>Fe<sub>2-x</sub>O<sub>4</sub>) nanoparticles gave rise to higher photocatalytic activities than NiFe<sub>2</sub>O<sub>4</sub>. The (NiAl<sub>0.15</sub>Fe<sub>1.85</sub>O<sub>4</sub>) photocatalyst led to the highest degradation rate, i.e. 76.2 % after 140 min of visible light irradiation, whereas NiFe<sub>2</sub>O<sub>4</sub>, NiAl<sub>0.05</sub>Fe<sub>1.95</sub>O<sub>4</sub> and NiAl<sub>0.10</sub>Fe<sub>1.90</sub>O<sub>4</sub> samples yielded decomposition rate of 62.67 %, 67.91 % and 74.12 % respectively (Fig. 10b). To study the kinetics of photocatalytic reactions, Langmuir- Hinshelwood model was investigated as follows [61]:

$$r = -dc/dt = Kkc / (1 + KA) \quad [5]$$

Where **r** is the rate of reaction (mol/L·min), **A** is the equilibrium concentration of the reagent (mol/L), **t** is the time (min), **k** is the rate constant (L/min), and **K** is the Langmuir constant (L/mol). This equation can be simplified to the following pseudo-first-order expression when the concentration of reagent being reacted is too low [62]:

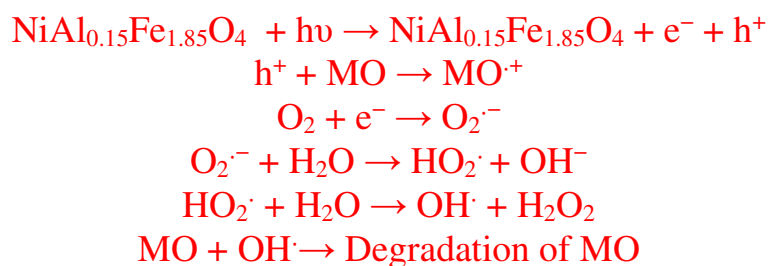
$$r = -dc/dt = kapp A \quad [6]$$

Integrating Eq. [6] results in:

$$\ln (A_t/A_0) = k_{app} t \quad [7]$$

Where  $k_{app}$  is the pseudo-first-order rate constant (L/min),  $t$  is the irradiation time (min),  $A_t$  and  $A_0$  are dye concentrations (mol/L) at instants  $t$  and  $t = 0$ , respectively, [63]. To explore the order of photocatalytic reactions, plots  $\ln (A_t/A_0) = f(\text{time})$ . By considering the linear relation between  $\ln (A_t/A_0)$  with time and negative slope of them, it can be said that these reactions were first-order (Fig. 10c).

The mechanism of photocatalytic activity of synthesized compounds for example  $\text{NiAl}_{0.15}\text{Fe}_{1.85}\text{O}_4$  nanoparticles in the degradation of methyl orange (MO) dye is given below [64-68]:



#### 4. Conclusion

In summary, Al-substituted nickel ferrite have been successfully prepared via a facile low-cost co-precipitation method. The TGA showed three mass losses, whereas DTA resulted in three endothermic peaks. The Rietveld refined XRD studies clearly showed the formation of single phase spinel structure. The lattice parameter is found to decrease with increasing aluminum content. TEM and SEM observations indicate cubic-shaped nanoparticles of  $(\text{NiAl}_x\text{Fe}_{2-x}\text{O}_4)$ . The crystalline particle size was found that in the range of 28 - 36 nm. FT-IR spectroscopy study shows 2 main metal oxygen bonds (Fe-O and M-O) at in the range of 400-600  $\text{cm}^{-1}$  confirming the creation of single phase spinel ferrite. The Raman spectra shows five Raman active modes ( $A_{1g} + E_g + 3T_{2g}$ ) which are expected in the spinel structure and Raman spectra has a very good agreement with reported data. In addition, the optical study showed that the

compounds have an optical band gap between 1.60 and 1.89 eV. Mössbauer spectra elucidate the nature of the phases and cation distribution. From the hysteresis loop, it is clear that the prepared samples can be control, for the  $(\text{NiAl}_x\text{Fe}_{2-x}\text{O}_4)$  nano-ferrites. Furthermore, the photocatalytic activities of  $\text{NiAl}_x\text{Fe}_{2-x}\text{O}_4$  nanoparticles were evaluated by studying the photodegradation of MO dye as model organic pollutant. The best photocatalytic activity was reached with the  $\text{NiAl}_{0.15}\text{Fe}_{1.85}\text{O}_4$  sample due to lower crystallite size and improved light harvesting capability.

### ***Acknowledgments***

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## Table captions

**Table 1.** Results of the Rietveld refinement of the X-ray diffractograms and crystallite size ( $D_{\text{XRD}}$ ) of the as-prepared samples

**Table 2.** The optical band gap of  $\text{NiAl}_x\text{Fe}_{2-x}\text{O}_4$

**Table 3.** Mossbauer's parameters of  $\text{NiAl}_x\text{Fe}_{2-x}\text{O}_4$  nanoparticles

**Table 4.** Magnetic properties of  $\text{NiAl}_x\text{Fe}_{2-x}\text{O}_4$  nanoparticles at room temperature

## Figure captions

**Fig. 1.** TGA and DTA curves for the as-prepared ferrite  $\text{NiAl}_{0.05}\text{Fe}_{1.95}\text{O}_4$

**Fig. 2.** The Rietveld analysis of X-ray diffraction patterns for  $\text{NiAl}_x\text{Fe}_{2-x}\text{O}_4$  ferrites with different amounts of aluminum substitution: (a)  $x=0.00$ , (b)  $x=0.05$ , (c)  $x=0.10$  and (d)  $x=0.15$ .

**Fig. 3a.** Shift in  $2\theta$  with increasing Al concentration.

**Fig. 3b.** Variation of lattice parameter (a) and the average crystallite size ( $D_{\text{XRD}}$ ) with Al concentration for  $\text{NiAl}_x\text{Fe}_{2-x}\text{O}_4$  with  $x = (0.00, 0.05, 0.10, \text{ and } 0.15)$

**Fig. 4a.** TEM images of the prepared samples

**Fig. 4b.** SEM images of the prepared samples

**Fig. 5.** FT-IR spectra of synthesized compounds calcined at  $700\text{ }^\circ\text{C}$

**Fig. 6.** Raman spectra of the nanoparticles  $\text{NiAl}_x\text{Fe}_{2-x}\text{O}_4$

**Fig. 7a.** Tauc plot obtained from UV-Vis DRS spectra of  $\text{NiAl}_x\text{Fe}_{2-x}\text{O}_4$  synthesized from the chemical co-precipitation method

**Fig. 7b.** The variation of the band gap energy ( $E_g$ ) as a function of Al concentration

**Fig. 8.** Mössbauer spectra of the samples

**Fig. 9a.** Hysteresis loops of the prepared ferrites at room temperature

**Fig. 9b.** The variation of the saturation magnetization ( $M_s$ ) and the coercivity ( $H_c$ ) values with varying aluminum substitution amounts

**Fig. 10a.** Photodegradation kinetics of MO dye in the presence of  $\text{NiAl}_x\text{Fe}_{2-x}\text{O}_4$  nanoparticles

**Fig. 10b.** Bar diagram for the % degradation of MO dye in the presence of  $\text{NiAl}_x\text{Fe}_{2-x}\text{O}_4$  nanoparticles

**Fig. 10c.** The pseudo first order kinetics of degradation of Methyl Orange dye

Figures :

Fig. 1

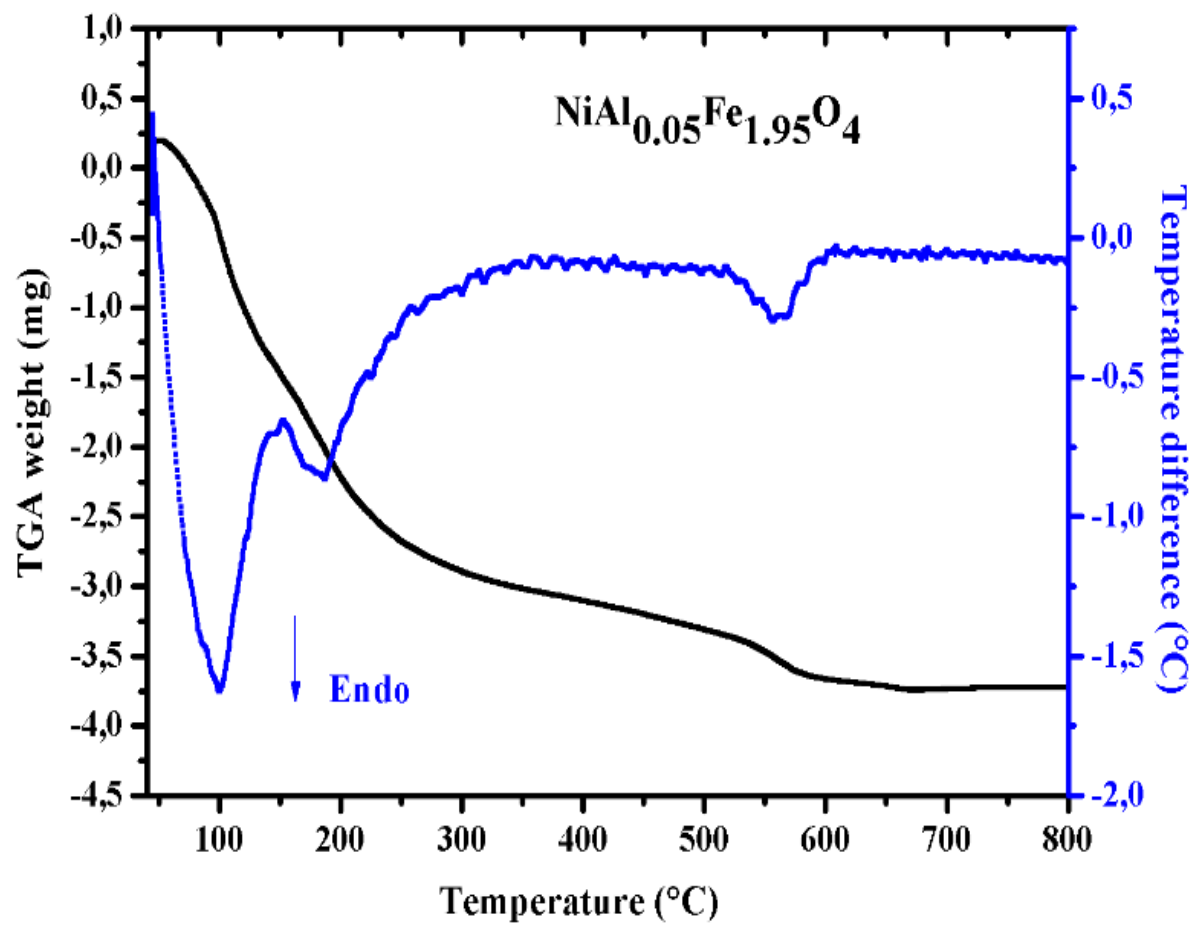


Fig. 2

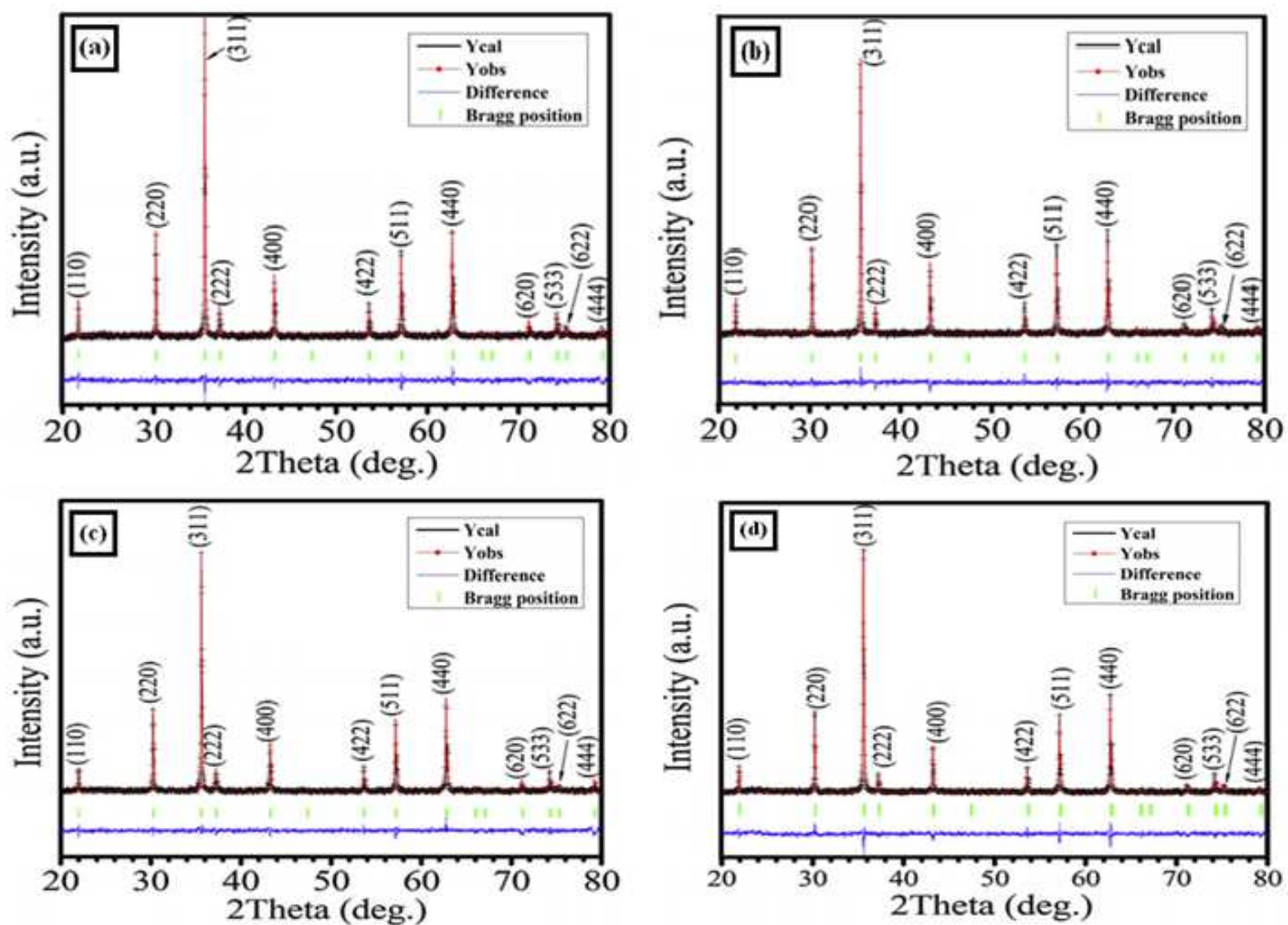


Fig. 3a

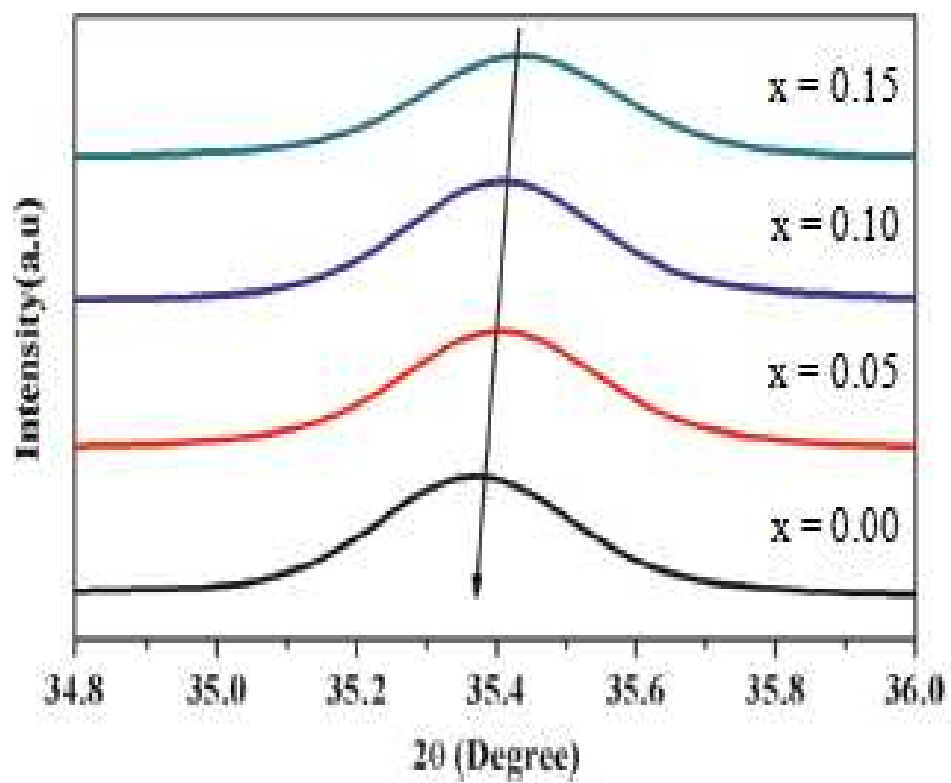


Fig. 3b

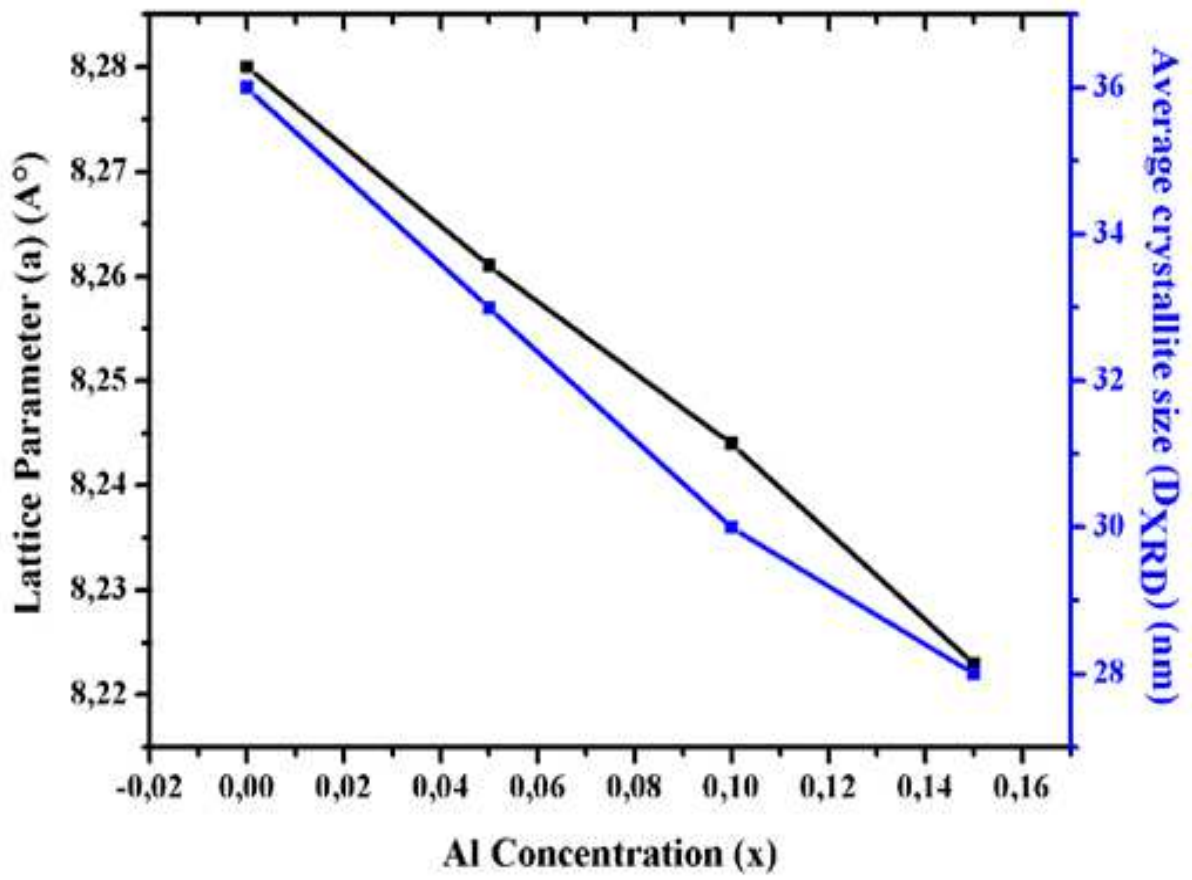


Fig. 4a

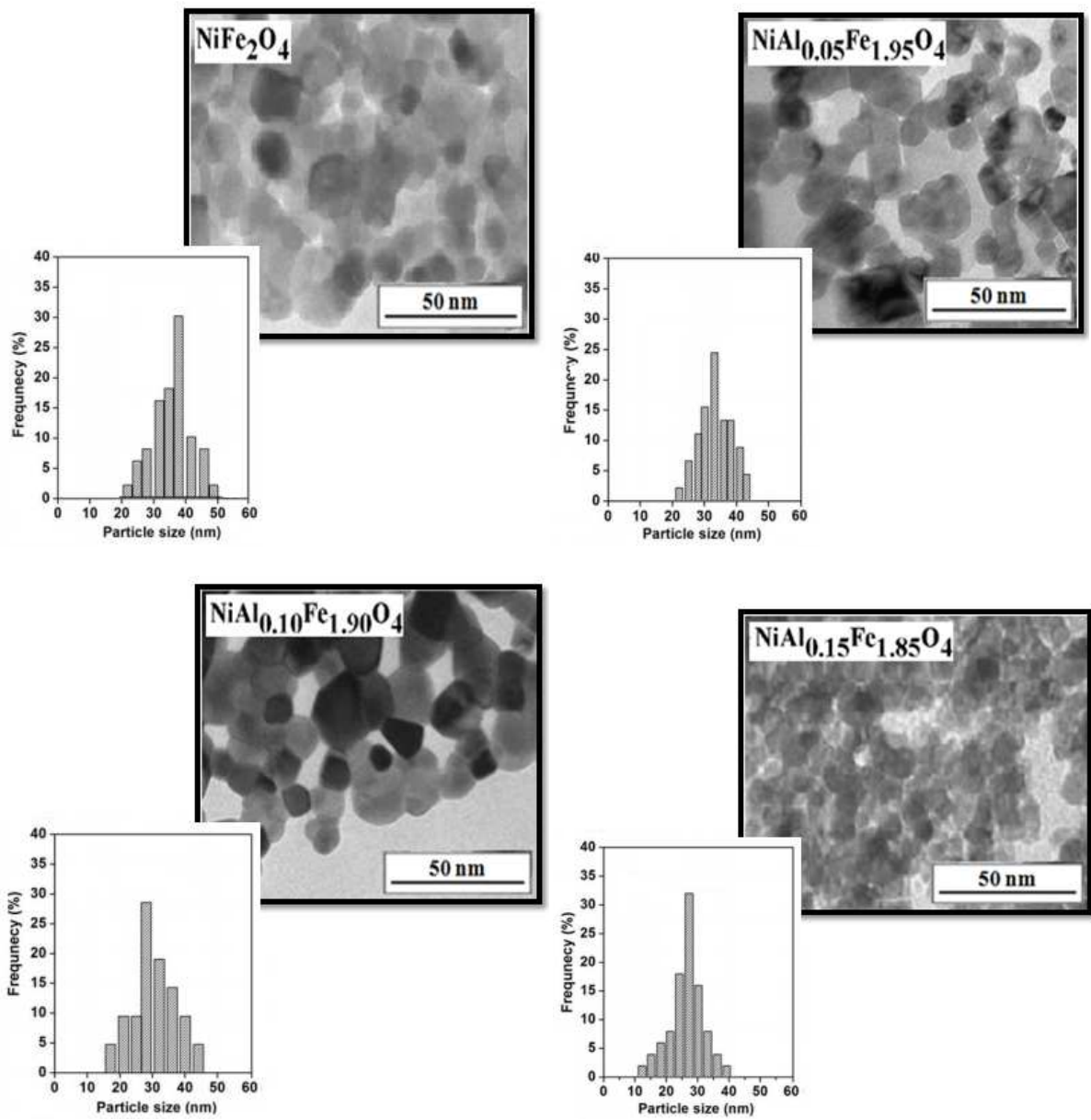




Fig. 4b

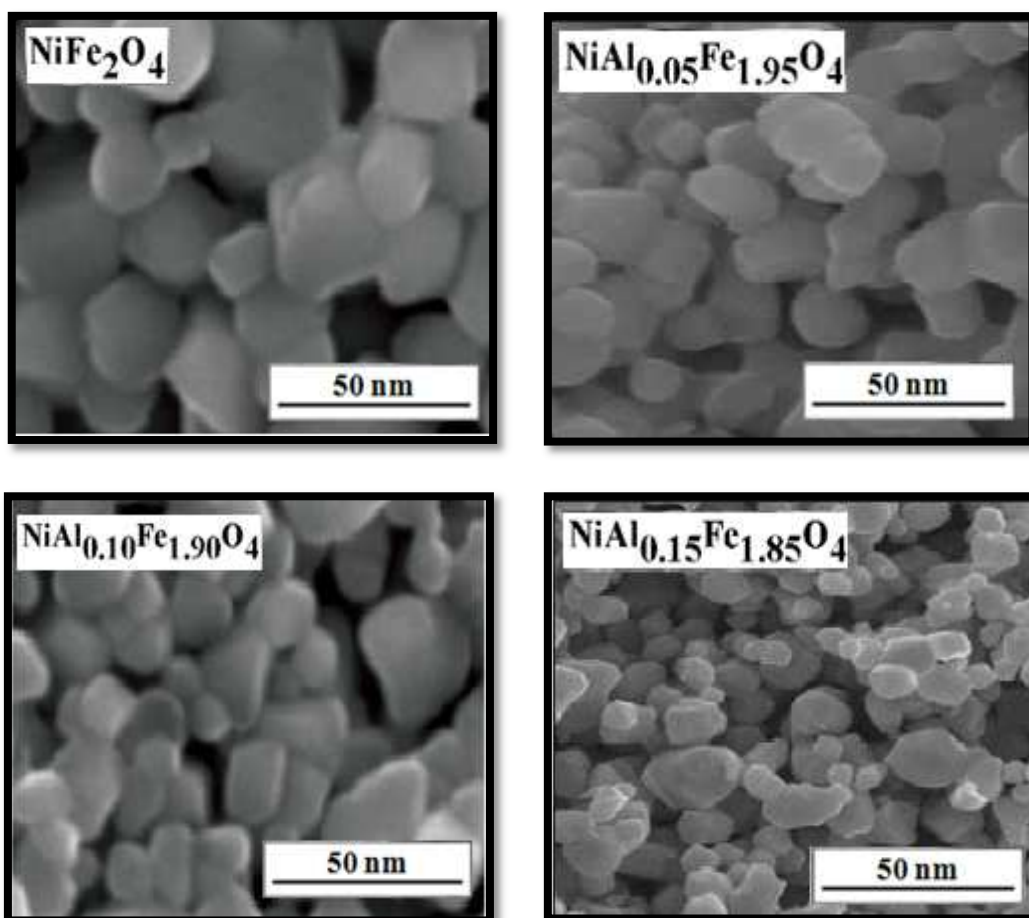


Fig. 5

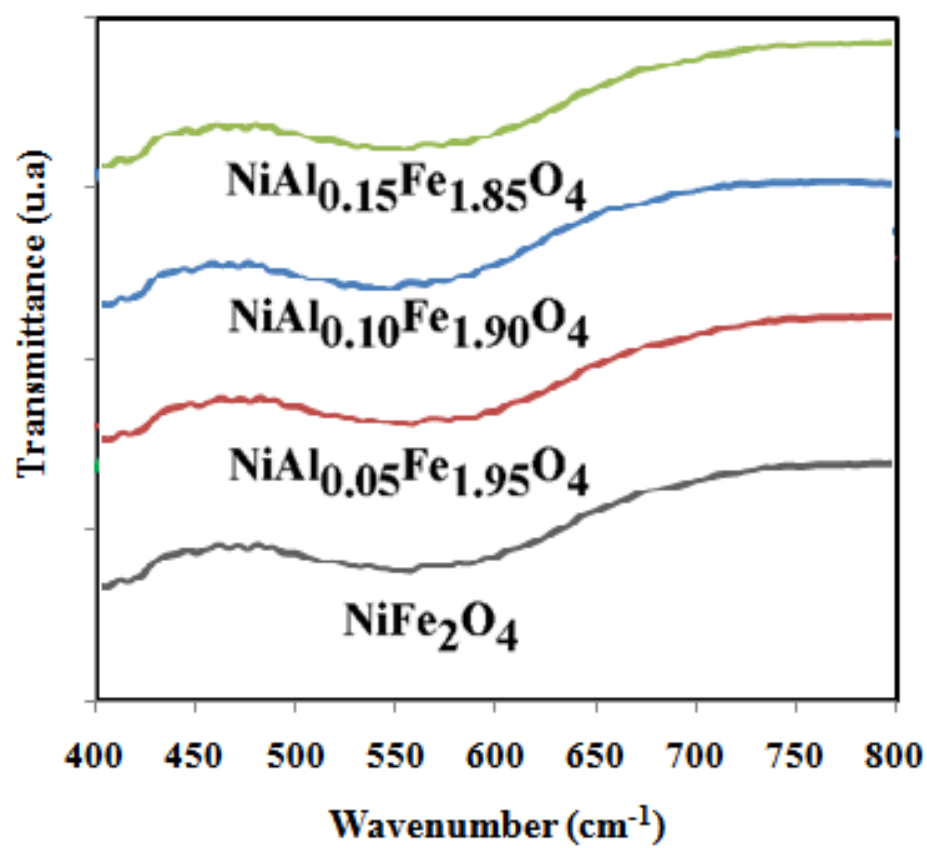


Fig. 6

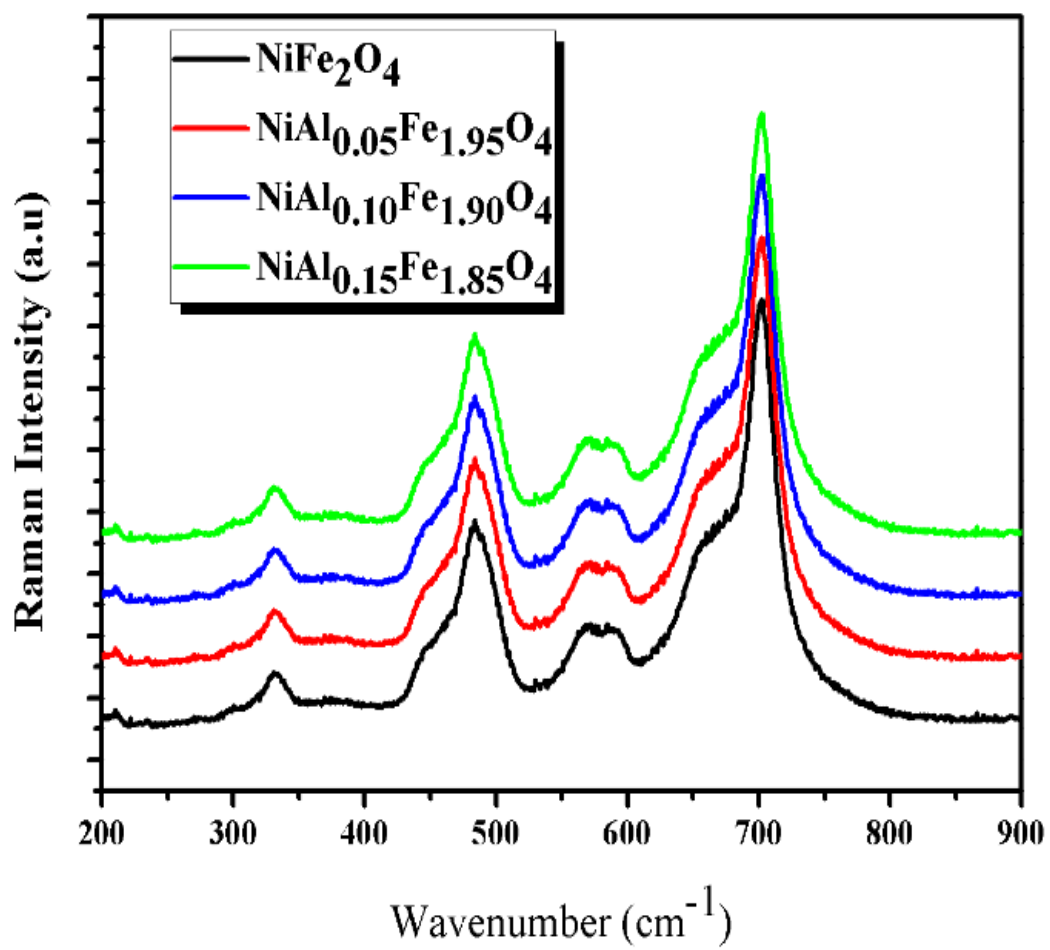


Fig. 7a

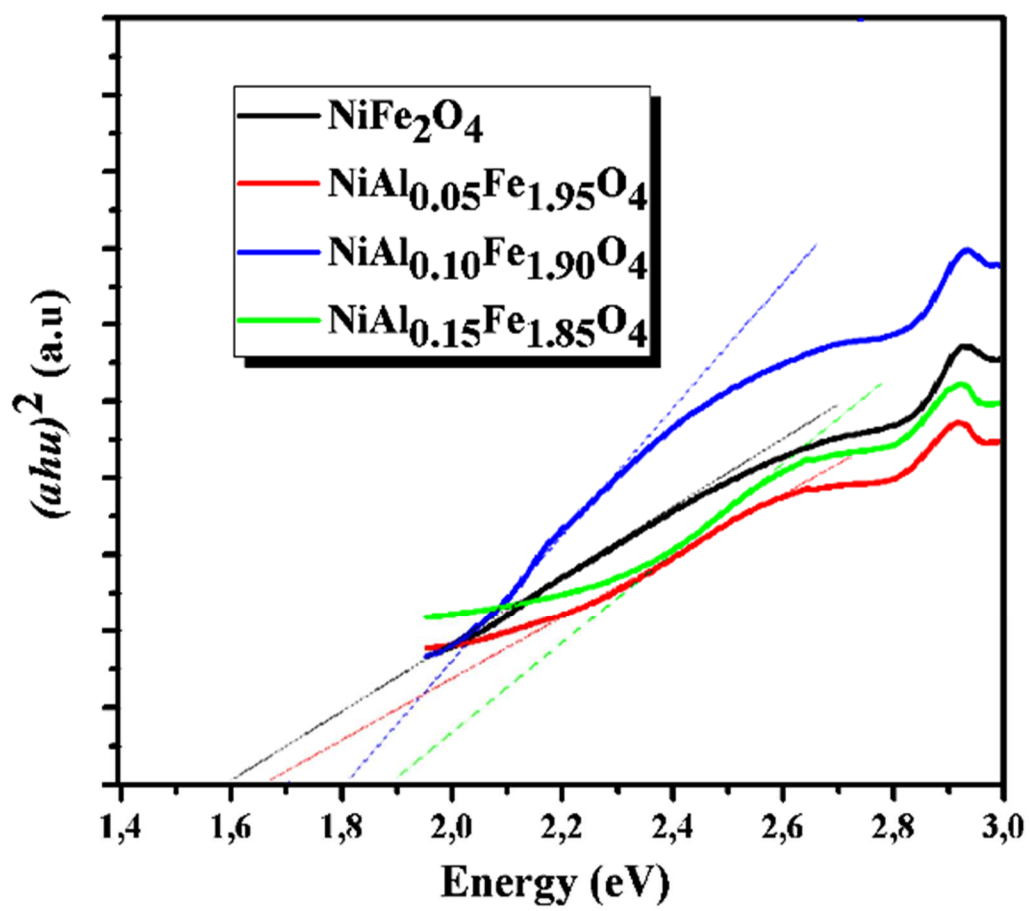


Fig. 7b

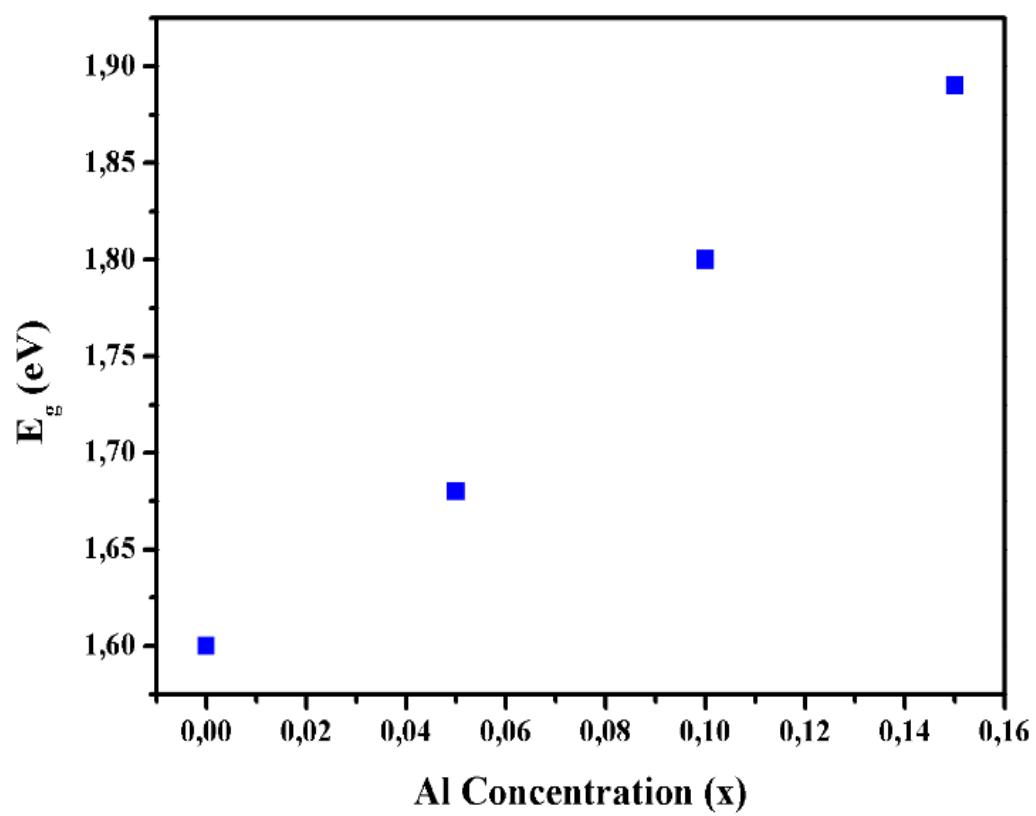


Fig. 8

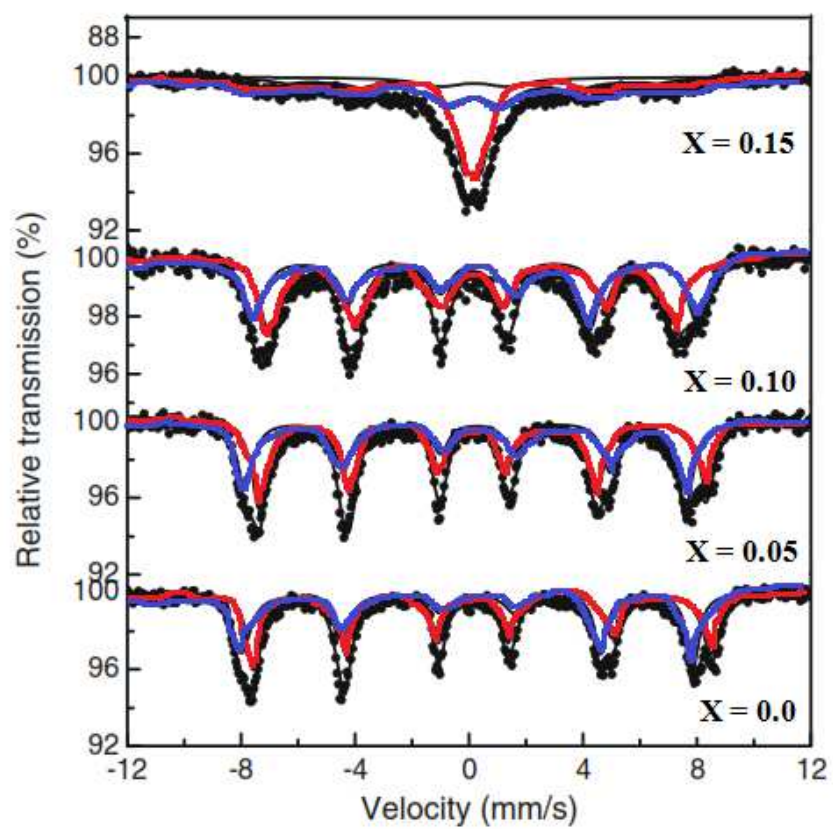


Fig. 9a

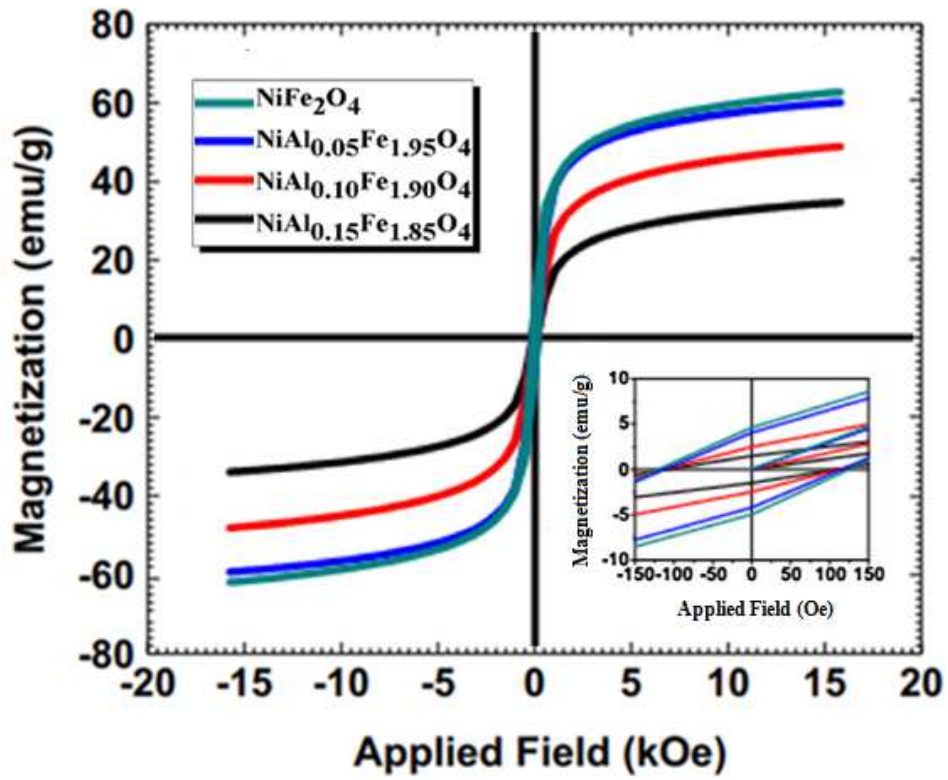


Fig. 9b

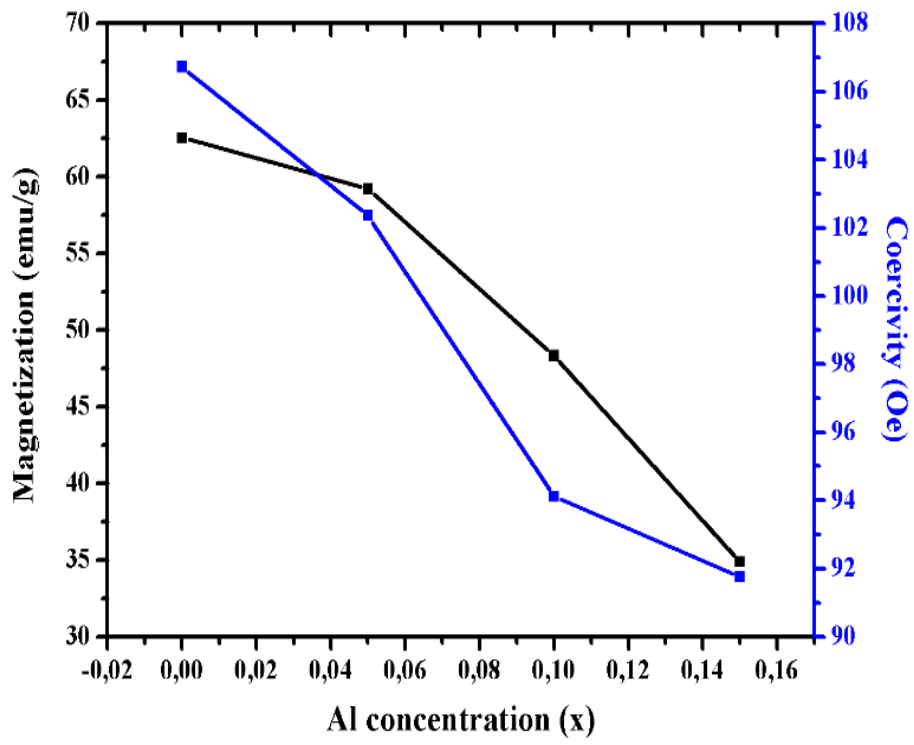




Fig. 10a

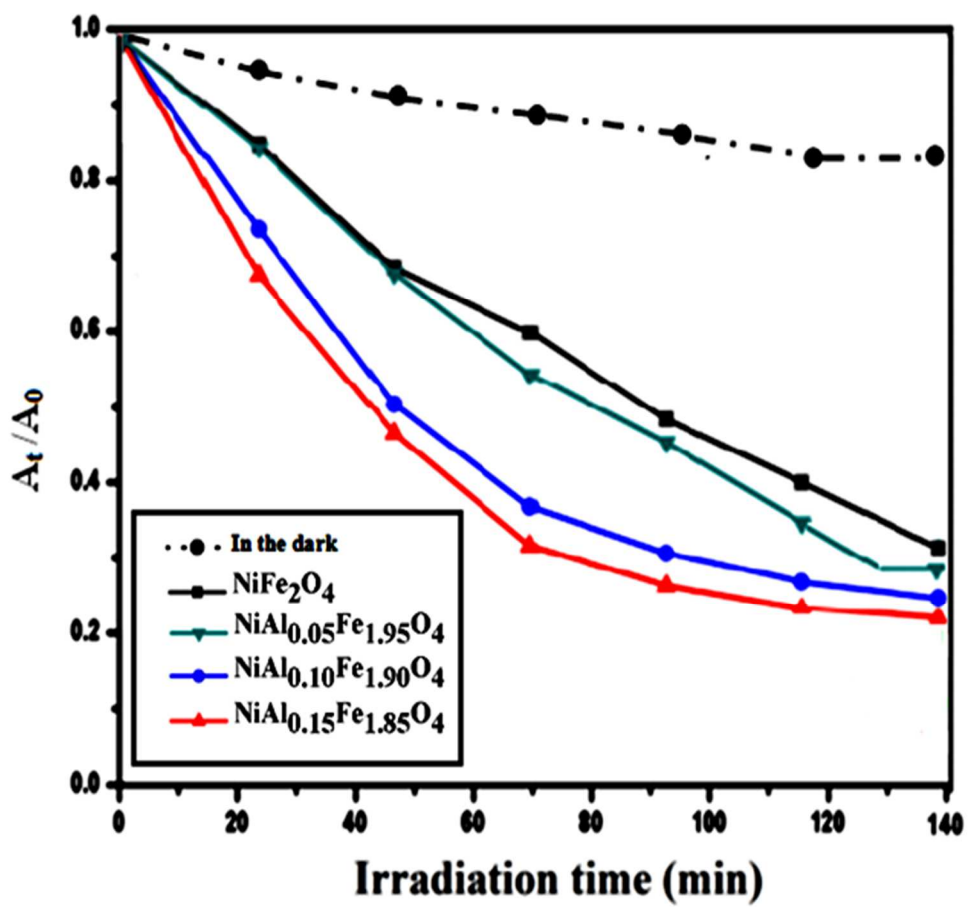


Fig. 10b

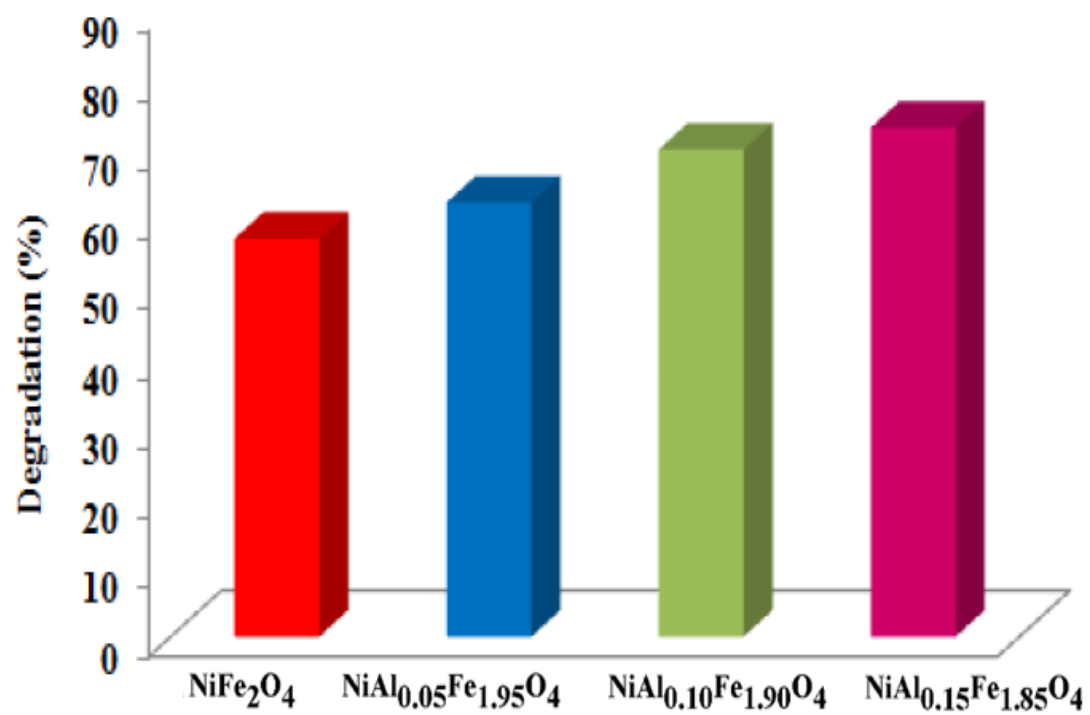
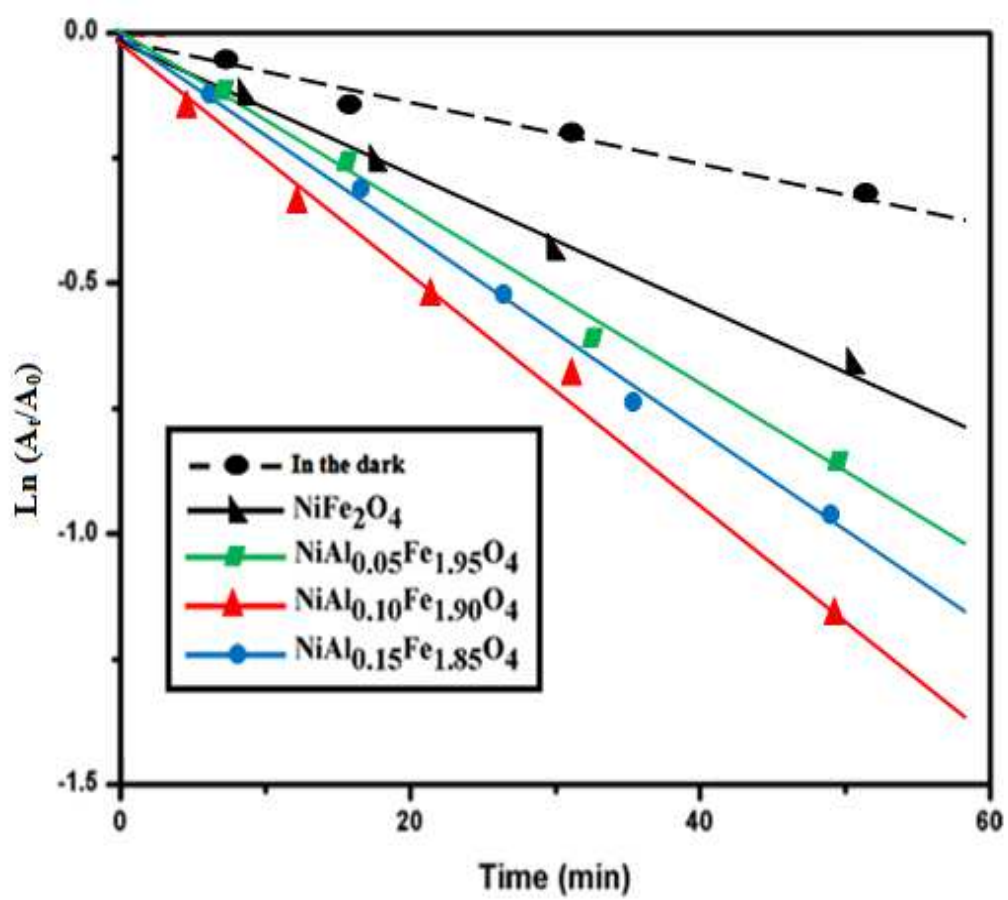


Fig. 10c



**Table****Table 1**

<b>Samples</b>	<b>Space group</b>	<b>a (Å)</b>	<b>V (Å<sup>3</sup>)</b>	<b>D<sub>XRD</sub> (nm)</b>	<b>R<sub>wp</sub></b>	<b>R<sub>p</sub></b>	<b>χ<sup>2</sup></b>
<b>NiFe<sub>2</sub>O<sub>4</sub></b>	Fd-3m	8.280	567.663	36	1.89	1.58	1.34
<b>NiAl<sub>0.05</sub>Fe<sub>1.95</sub>O<sub>4</sub></b>	Fd-3m	8.261	563.764	33	1.59	1.23	1.24
<b>NiAl<sub>0.10k</sub>Fe<sub>1.90</sub>O<sub>4</sub></b>	Fd-3m	8.244	560.291	30	2.01	1.59	1.59
<b>NiAl<sub>0.15</sub>Fe<sub>1.85</sub>O<sub>4</sub></b>	Fd-3m	8.223	556.696	28	1.45	1.38	1.08

**Table 2**

<b>Samples</b>	<b>Optical band gap 'E<sub>g</sub>' (eV)</b>
<b>NiFe<sub>2</sub>O<sub>4</sub></b>	1.60
<b>NiAl<sub>0.05</sub>Fe<sub>1.95</sub>O<sub>4</sub></b>	1.68
<b>NiAl<sub>0.10</sub>Fe<sub>1.90</sub>O<sub>4</sub></b>	1.80
<b>NiAl<sub>0.15</sub>Fe<sub>1.85</sub>O<sub>4</sub></b>	1.89

**Table 3**

<b>x</b>	<b>Component</b>	<b>IS (mm/s)</b>	<b>QS (mm/s)</b>	<b>Hf (KOe)</b>	<b>HWHM (mm/s)</b>	<b>AREA (%)</b>
<b>0.15</b>	Tetrahedral	0.21	0.02	379	0.85	40.8
	Octahedral	0.26	0.04	446	0.85	26.1
	Double	0.23	0.58	-	0.40	33.1
<b>0.10</b>	Tetrahedral	0.21	0.03	439	0.40	57.8
	Octahedral	0.33	0.01	481	0.41	42.2
<b>0.05</b>	Tetrahedral	0.24	0.02	464	0.31	55.1
	Octahedral	0.36	0.03	502	0.34	44.9
<b>0.00</b>	Tetrahedral	0.24	0.02	479	0.26	49.6
	Octahedral	0.37	0.01	511	0.39	50.4
Errors	-	±0.01	±0.01	±1	±0.01	±0.2

**IS** is the isomer shift, **QS** is the quadrupole splitting, **Hf** is the magnetic hyperfine field, **HWHM** is the half width at half maximum, and **AREA** is the absorption area.

**Table 4**

<b>Samples</b>	<b>M<sub>s</sub> (emu/g)</b>	<b>M<sub>r</sub> (emu/g)</b>	<b>H<sub>c</sub> (Oe)</b>
<b>NiFe<sub>2</sub>O<sub>4</sub></b>	62.54	4.83	106.72
<b>NiAl<sub>0.05</sub>Fe<sub>1.95</sub>O<sub>4</sub></b>	59.21	4.07	102.36
<b>NiAl<sub>0.10</sub>Fe<sub>1.90</sub>O<sub>4</sub></b>	48.33	2.48	94.12
<b>NiAl<sub>0.15</sub>Fe<sub>1.85</sub>O<sub>4</sub></b>	34.87	1.21	91.76

## Synthesis of Spinel ferrites $\text{NiAl}_x\text{Fe}_{2-x}\text{O}_4$ through co-precipitation method

