Structural characterization of rare earth Nd^{3+} Substituted Ni-Zn Nano Ferrites and applications

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Abstract: $Ni_{0.8}Zn_{0.2}Nd_xFe_{2-x}O_4$ (where x=0.000 to 0.040 with step of 0.010) were ecofriendly synthesized by Citrate-Gel Auto Combustion method at lower temperature. The synthesized powders were sintered and characterized by XRD, SEM with EDS, FTIR and UV-Spectroscopy analysis of Prepared samples were confirmed the Single-Phase Cubic Spinel Structure. The observed results can be explained on the basis of composition and crystal size. Crystallite Size (D) of prepared ferrites were in the range of 12-22nm. SEM all micrograph images are present grains size, these are having maximum homogeneous dispensation and agglomeration between inter particles. The FTIR spectroscopic results, it is clear that ν_1 is in the range of 553-574 and ν_2 in the range of 391-422 which conclude the cubical spinel structure. The band gap energy is increased with increasing of Ce Substitution, i.e 2.48 to2.57ev.

Keywords: Nano-ferrites; XRD; SEM and EDS: UV Spectroscopy

1.INTRODUCTION:

Synthesis of nano-ferrites, especially spinel ferrites, characterized by a low size distribution is important due to their remarkable electrical and magnetic properties and wide practical applications in information storage systems, ferro-fluid technology, magneto caloric refrigeration and medical diagnostics [1-2]. The electrical properties of ferrites depend upon several factors including the route of preparation, composition of constituents, grain structure or size and the amount and type of substitution [3]. Ferromagnetism is supported by electron spin and the material acts as a powerful magnet. They are widely used in industry and devices like electric motors, generators, transformers, telephone, loudspeakers, magnetic stripe in credit cards. The main advantage of ferrites is its compositional variability of very high degree. Nano-particle ferrites play significant role in view of their extensive applications. Their physical and chemical properties remarkably differ from their bulk counterparts making them highly potential for different technical applications. Grain boundaries control their transport properties instead of grain itself [4]. Spinel ferrites are commercially important materials due to their excellent magnetic and electric properties [5] One important characteristic of ferrites is their high values

of resistivity, low magnetic and dielectric losses [6] Due to this reason, the magnetic materials have explored a wide range of applications and replacing conventional materials. The Conventional solid-state reaction route is widely used for the production of ferrite because of the low cost and suitability for the largescale production.

One of the most important advantages of ferrites is their very high degree of compositional variability. Nanoparticles of ferrites are very important group of magnetic materials due to their extensive use in a wide range of applications. The properties of nano materials are remarkably different from that of their bulk counterpart. The interest in ferrite nano particles is due to their important physical and chemical properties and potential for various technological applications such as highdensity magnetic storage, electronic and microwave device, sensors, magnetically guided drug delivery. Grain boundaries control their transport properties instead of grain itself [7]. Different chemical methods can be used to obtain high level molecular mixing, chemical homogeneity etc. while synthesizing spinel ferrites [8-11]. Synthesis of Nickel-Zinc-Copper ferrites using ceramic, refluxing, combustion, hydrothermal, reverse micelle, co-precipitation, micro emulsion, ball milling and spark plasma sintering methods were already reported [12-19]. The present work reports some of the results obtained related to synthesized Ni-Ce-Zn ferrites such as XRD analysis, SEM-EDS, FTIR, UV spectroscopy.

2.Experimental techniques:

Nd^{3+} substituted Ni-Zn ferrites of chemical formulation $Ni_{0.8}Zn_{0.2}Nd_xFe_{2-x}O_4$ were synthesized by Citrate-Gel Auto Combustion Figure1.Stiochiometric amounts of metal nitrates of nickel, cerium, ferric and zinc of 99% purity are dissolved in distilled water and later mixed with citric acid in 1:1ratio. This mixture after stirring was heated to 80^oC and by adding ammonia the solutions pH value was set to 7 to form a sol. The resulting solution was made to form a viscous gel on stirring and heating between 180^OC-200 ^0C to result in ferrite powder. This ferrite powder was grinded using Agate Mortar and calcinated for four hours at 500^0C.This powder was mixed with 10% polyvinyl alcohol (PVA) and pressed to form pellets by applying pressure of 10-ton cm^{-2}. The pellets were finally sintered and coated with silver paste to provide electrical contact.

X-ray diffraction is an analyse the crystal structure, in these process crystalline phases, orientation and crystal alignments. The strongest reflection has come from (311) peak for every sample. The crystalline size of all samples was calculated from the Half Width at Full Maximum (HWFM) of the (311) reflection peak in the XRD pattern using Debye-Scherrer's formula [20].

Scherrer Formula:

$$\text{Crystalline size of the sample } D = \frac{0.91\lambda}{\beta \cos\theta}$$

Where λ =wavelength of X-ray used

B= Full Width Half Maxima (FWHM) in radians.

θ = peak position.

Lattice parameter(a) of the sample was calculated by the formula

$$a = d * (h^2 + k^2 + l^2)^{1/2}$$

Where a= Lattice Constant

(hkl) are the Miller Indices

d = inter planner spacing,

The X-ray density $dx = \frac{nM}{a^3N}[g/cm^3]$ [21]

Where M = molecular weight of the sample

n =number of molecules in a unit cell of spinel lattice.

a =lattice parameter and N is the Avogadro number.

The Volume of the Unit Cell V= a^3

During absorption energy is absorbed by the molecules of electron in uv or visible form of light and this electron gets excited to higher orbit [22]. The band gap energy was calculated by using the formula

$$E=\frac{hc}{\lambda} \text{ (or) } E=\frac{1240}{\lambda}$$

3.Result and Discursion:

XRD analysis:

XRD pattern was confirm single phase cubic spinel structure for (111), (220), (311), (222), (400), (422), (511) and (440) planes which matches with standard pattern JCPDS file number-48-0489. XRD patterns of the prepared Ce substituted Ni-Zn ferrite sample was displayed in Figure **1.**

lattice parameter, crystallite size, volume and x-ray density of all samples show in Table 1 It is clearly indicated that the crystallite size ranges between 12.8 nm to 22.7 nm.

The gradual inconsequence's increase in the crystalline size with the increase in the cerium dopant into the single-phase cubic spinel lattice. Since the ionic radius of Nd^{3+} (1.33 Å) is larger than that of the Fe^{3+} ion (0.64 Å), it should occupy an enormous area in the B site than the A site. It results in the curtailment of grain growth and also decreases the crystallite size of $Ni_{0.8}Zn_{0.2}Nd_xFe_{2-x}O_4$ ($x \leq 0.000 \leq 0.040$) nano crystalline particles [29]. Lattice parameters decrease with increased Ce concentration obeying Vegard's law [30]. X-ray density was observed to increase with increased Ce concentration since x-ray density depends on the molecular weight and lattice parameter of the sample. Volume of the unit cell also decreased since it depends on lattice parameter. It is also observed that experimental density less than X-ray density of the sample.

Table 1. Crystalline size, Lattice Parameter, X-ray density & Volume

$Ni_{0.8}Zn_{0.2}Nd_xFe_{2-x}O_4$	M.W (gm/ mol)	Crystallite size(nm)	Lattice constant (A^o)	X-ray density(d_x) (gm/cc)	Volume $(A^o)^3$	Ex. density(d_e)(gm/cc)
X=0.000	239.73	22.7	8.40	5.35	594.2	3.2
X=0.010	240.57	18.4	8.46	5.27	605.4	3.5
X=0.020	241.42	19.3	8.45	5.30	603.3	3.6
X=0.030	242.26	12.8	8.39	5.43	590.5	3.9
X=0.040	243.10	19.3	8.42	5.39	596.9	4.0

The experimental density and lattice parameters of the prepared sample with Ce substituted compositions were shown in Figure 2&3

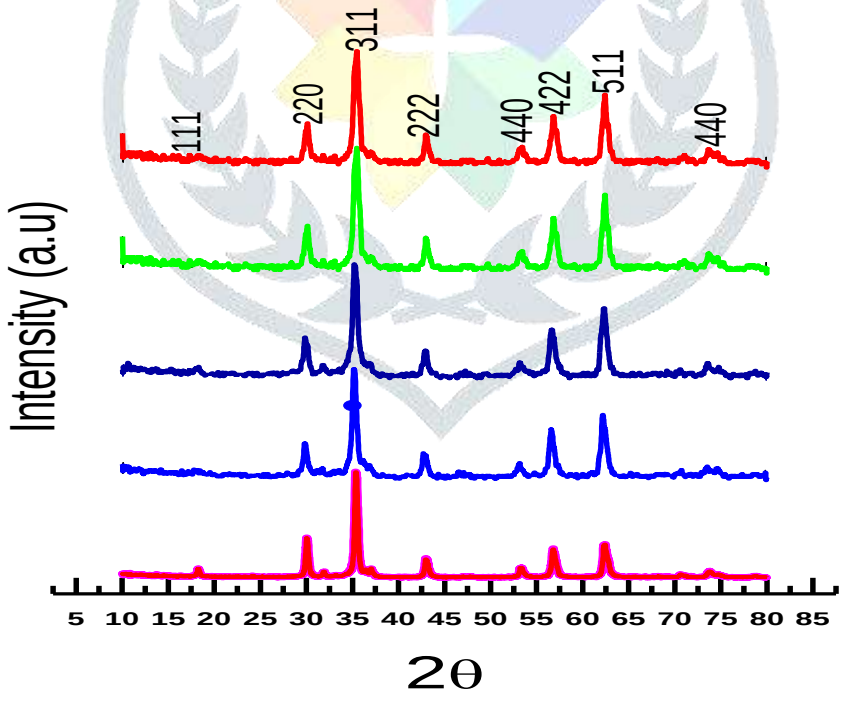
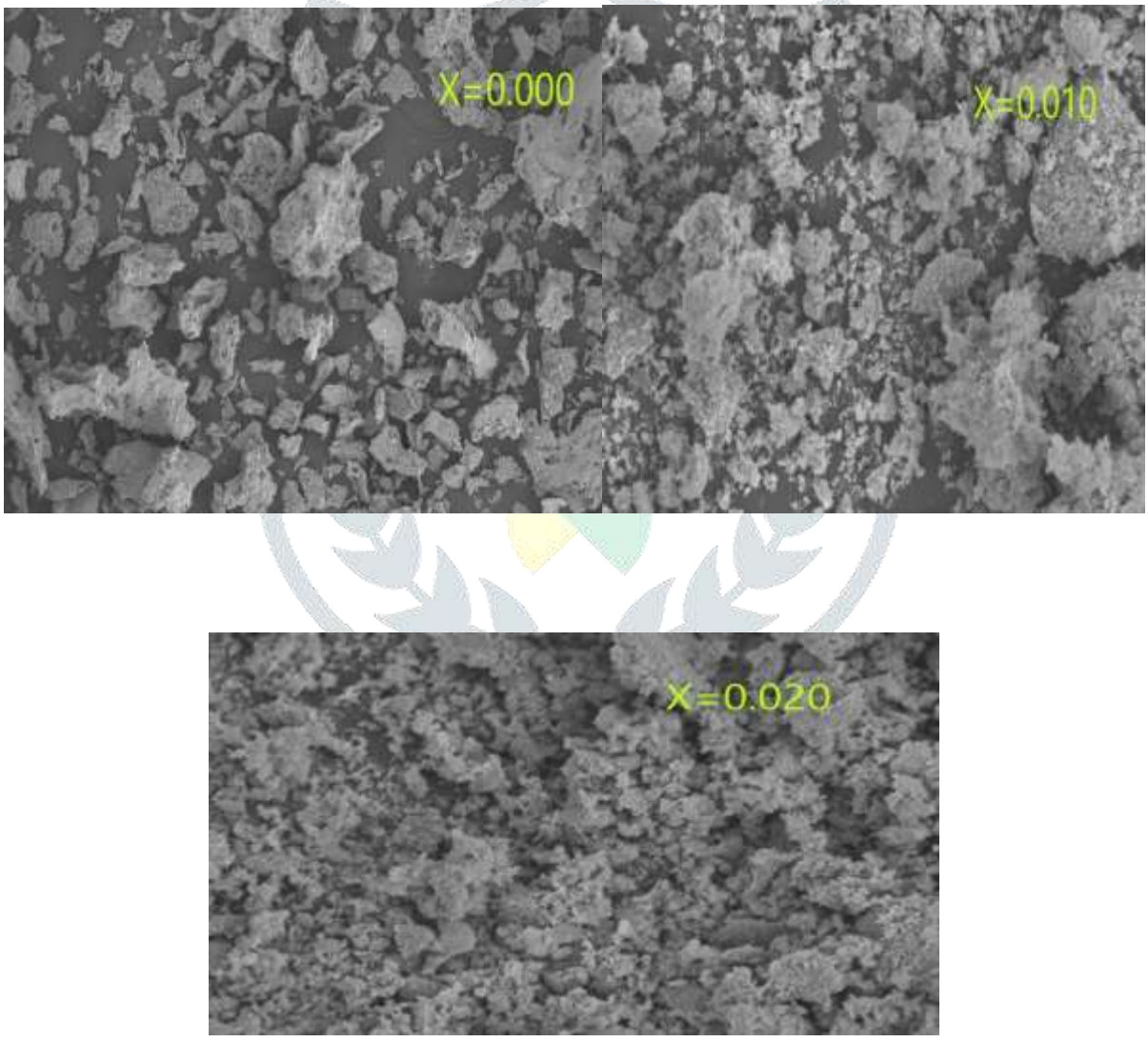


Figure 1.XRD Pattern of Nd Substituted Ni-Zn nano-ferrites

3.1 SEM micrographs:

Scanning Electron Microscopy (SEM) was result out the Micro structural analysis of the prepared sample. These representations were shown from the figure **4**. SEM all micrograph images are present grains size, these are having maximum homogeneous dispensation and agglomeration between inter particles. Finally conclude from the bellow micrographs of the ferrite all samples the grain size was nano meter range with shape of spherical and inter partials have narrow size dispensation. SEM image revealed that with increasing in the Nd concentration, when the increased Nd^{+3}substitution randomly in Ni-Zn ferrites then the grain size was inconsequence's increased except pure sample of the series its authentication from the XRD analysis.



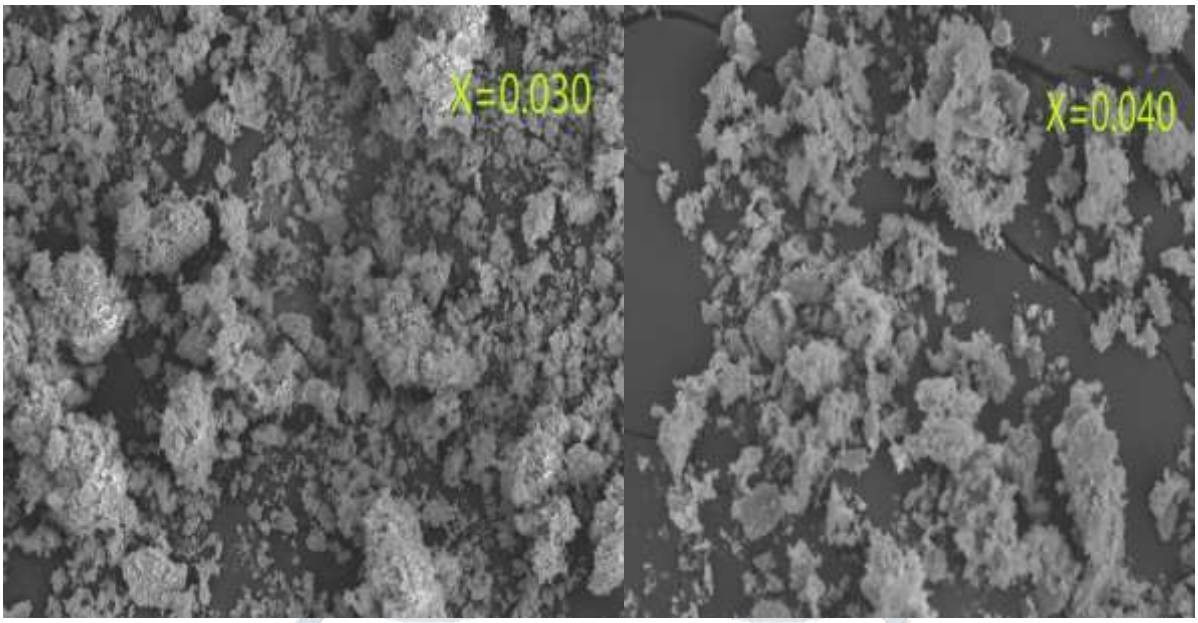


Figure 4 SEM Micrographs of Ni-Nd-Zn Nano ferrites

3.2 ELEMENTAL ANALYSIS EDS:

Analyze for the elemental percentage of Nd^{3+}substituted Ni-Zn ferrites by ED- spectroscopy. There series existence of elements (Nd, Zn, Ni, Fe and O) was detected without precipitating cations. Elemental percentage for all the prepared ferrites were communicate in figure **5**.

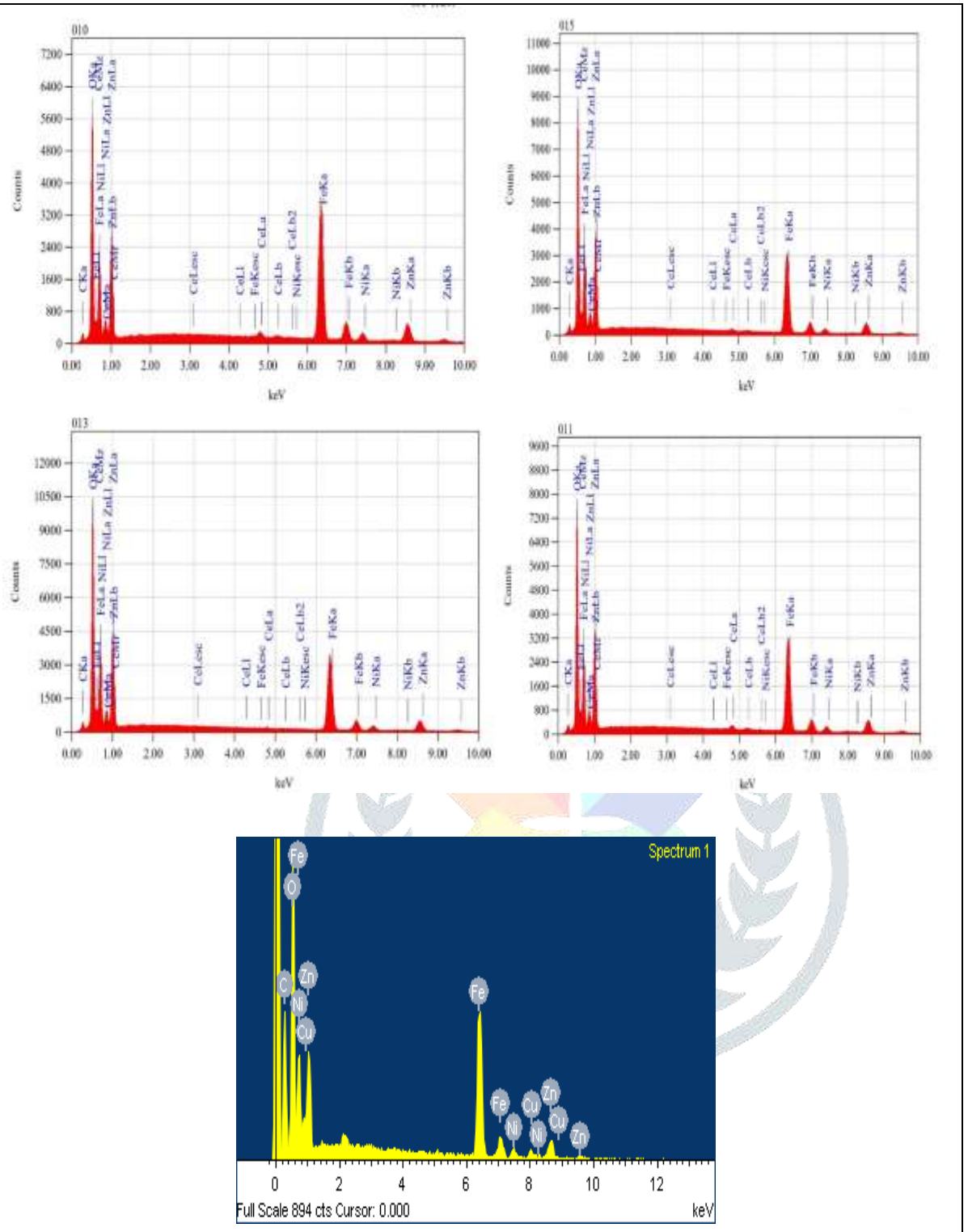


Figure 5. EDS Spectra of Ni-Nd-Zn Nano ferrites

3.3 FTIR spectral of nano crystalline:

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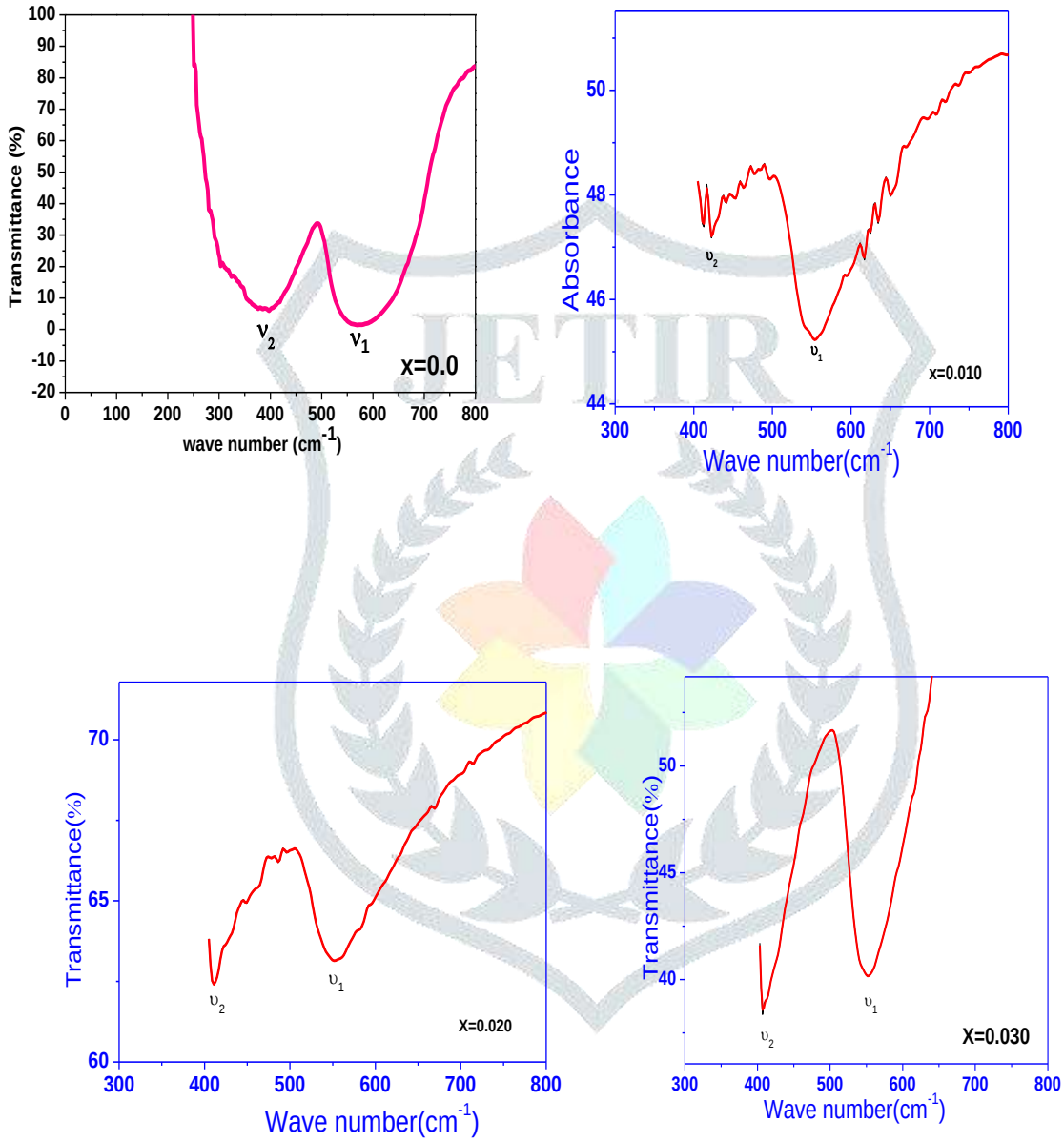

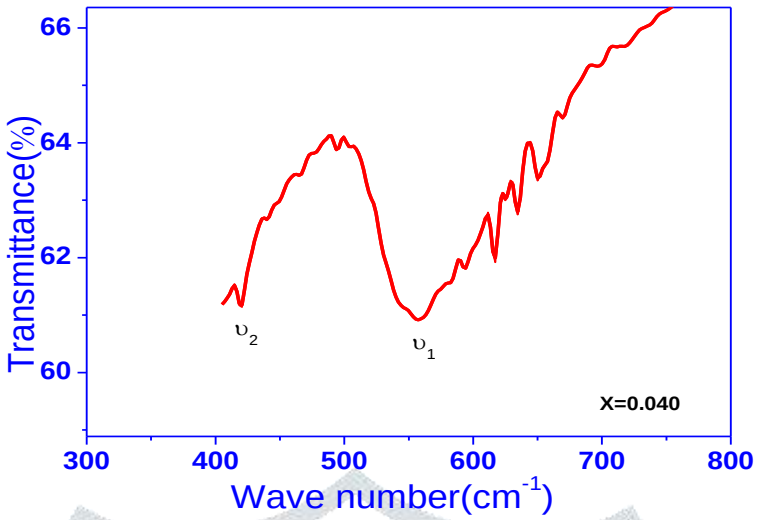

Figure 6. FTIR absorption spectrum of $Ni_{0.8}Zn_{0.2}Nd_xFe_{2-X}O_4$ nano ferrites

The FTIR spectra is cleared that the spinel structure with the formation two kinds of characteristic absorption bands found. These were associated with the straighten vibrations of tetrahedral (A) and octahedral (B) positions correspondingly, which confirm the cubical spinel structure.

Prepared samples were studied in the part of structural characterization Fourier Transform Infra-Red (FTIR) with frequency 200 to 600 cm^{-1}, plated in figure **6.**

Spectra were telling about characteristic features of ferro-spinel's, and absorption bands are ascribing to the stretching vibrations due to interactivity between the oxygen atom and the cations in tetra and octahedral. Variation of $\nu_1$and ν_2 absorption bands due it changes in bond length (Fe-O) at the octa and tetrahedral spinel structure. In table **2** as show The FTIR spectroscopic results, it is clear that ν_1 is in the range of 553-574 and ν_2 in the range of 391-422 which conclude the cubical spinel structure.

Table 2 FTIR absorption bands in the investigated samples

$Ni_{0.8}Zn_{0.2}Nd_xFe_{2-x}O_4$	v_1	v_2
X=0.000	574	391
X=0.010	553	422
X=0.020	551	410
X=0.030	553	405
X=0.040	557	418

3.4 Optical Studies by UV-DRS:

Optical studies connected to prepared nano-ferrites was execute taking BaSO4 as references. These analysis by using the technique of UV–DRS. During absorption, molecules of electron absorb energy in the form of uv or visible light exciting the electron to higher orbit [31]. Nd substituted Ni-Zn ferrites has wave length 499 nm and it is a visible region with absorbance verses wavelength.

Increase in Nd concentration decreases wavelength and the absorption edge shifts from 499 nm to 482 nm. In case of Nd substituted Ni-Zn ferrite for composition x=0.040 blue shift is observed which may be due to increase in particle size leading to expansion of band gap [32]. A wavelength of 499 nm was observed for particles under study in above Figure **7**.

The band gap energy is increased with increasing of Ce Substitution, i.e 2.48 to2.57ev, due to method of synthesis, density and lattice parameters of the samples. The observed values of cut off wave length and band gap energy were show in table **3.**

Table 3 $Ni_{0.8}$ $Zn_{0.2}$ Nd_x $Fe_{2-x}O_4$ nano ferrites Cut off wave length with Band gap energy

$Ni_{0.8}Zn_{0.2}Nd_xFe_{2-x}O_4$	Cut off wave length	Bandgap energy
X=0.000	499	2.484
X=0.010	494	2.510
X=0.020	490	2.530
X=0.030	486	2.551
X=0.040	482	2.572

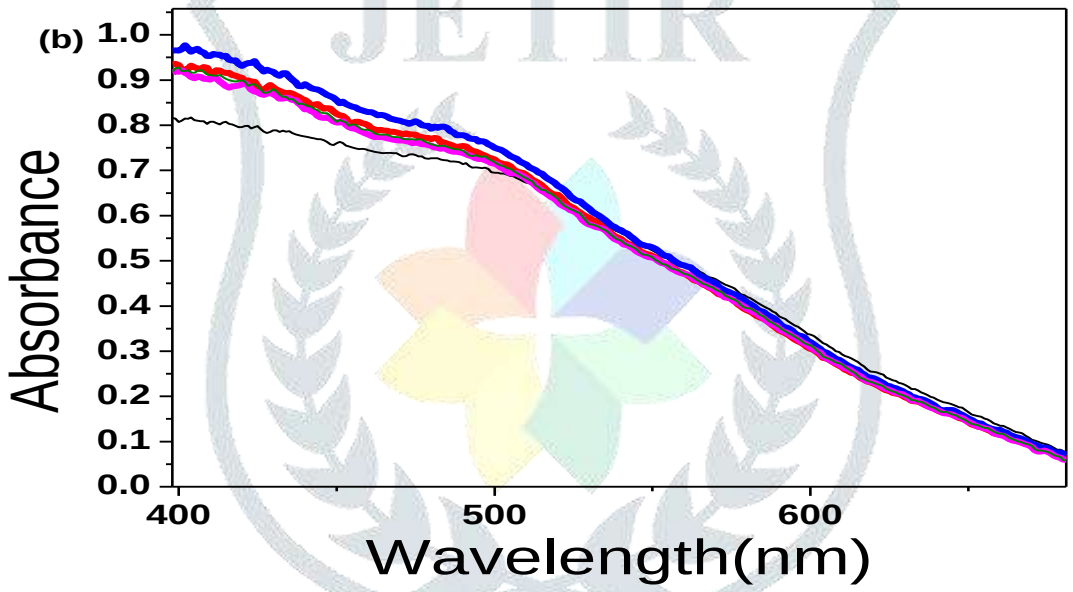

Figure 7. UV–visible spectra of nano-crystalline $Ni_{0.8}Zn_{0.2}Nd_xFe_{2-x}O_4$

4. Conclusions

X-ray diffraction pattern of the prepared samples confirms the formation of single phase cubic spinal structure. Ferrite's composition of $Ni_{0.8}Zn_{0.2}Nd_x$ $Fe_{2-x}O_4$ with an average crystallite size between 12 to 22 nm were synthesized through citrate Gel-Auto combustion method. Doping Nd in Ni-Zn ferrite system decrease lattice parameter and increase x-ray density's micrographs of the various compositions indicate the morphology of the particles was similar. They are largely agglomerated. The FTIR spectrum exhibited V_1 and V_2 fundamental bands, corresponding to octahedral and tetrahedral sites in the ferrite structure. Optical studies by UV–DRS decrease in wavelength with increase in Nd concentration. The absorption edge shifts from 499nm to 482nm.

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