Effect of Cerium substitution on the structural and optical properties of Co-Mg mixed nano ferrites by citrate gel auto combustion method

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Abstract: From citrate gel auto combustion method Ce co-doped Co-Mg mixed nano ferrites synthesized.The synthesized samples structural characterizations have been done by XRD, SEM, EDAX, FTIR, UV-VIS. Spectroscopy. From x-ray diffraction studies, reveals that synthesized samples are in crystalline nature, as well as in nano meter region, which is 13.15nm to 23.13nm. Lattice parameter andX-ray density increases with increasing Ce Concentration on Co-Mg Mixed nanoferrites. Morphology of the synthesized samples was studied using scanning electron microscope (SEM). The elemental analysis of all the Cu-Zn-Ce nano ferrite samples with different compositions was analyzed by Energy Dispersive Spectrometer (EDS). FTIR spectroscopy used to find the functional group analysis of the materials. Optical absorption behavior of the synthesized samples carried out by UV visible spectral analysis.The observed results can be explained on the basis of composition and crystal size.

Keywords: Citrate gel auto combustion method, XRD, SEM, FTIR, UV-vis.

INTRODUCTION: The ferrites are ferromagnetic materials, which can be classified into different classes it is obtained on their structure including spinals, garnets and hexagonal ferrites. The ferrite materials come under spinal ferrite regarding their various applications in several areas which contain storage devices, electrical devices MRI, microwave industry [1-3]. Ferrites also have a wild range of applications in the field of catalyst, sensors; magnetic devices etc[4,5]especially cobalt ferrites have significant applications among all other spinal ferrite systems. as a result of its unique properties that is high coercivity, high anisotropic value, highSquarencess ratio and moderate saturate magnetization[6-7]. Many researchers concentrated on earth metal doping on transition elements to enhance physical properties of ferrites. Magnetic mixed nano ferrite particles have significant role over the last few years. These nano particles are significantly used in electrical devices and high density magnetic recording[8]. Their low cost, high saturation magnetization high curie temperature and hysteresis loop properties make them excellent materials for high-density recording media, and microwave devices. The nano

magnetic particles have special properties as compared to the bulk because of the large volume fraction that atoms occupy at the grain boundary area, which in turn is responsible for several unusual properties like spin canting, surface anisotropy, paramagnetism super paramagnetism (sp), dislocations etc. This makes them quite flexible to tailor the material for specific applications [9]. Ferrites are extensively used in many kinds of magnetic devices such as transformers, inductors, magnetic heads, in resonance circuits for high frequency [10]. It was found that all rare-earth metal ions favor the occurrence of second phase, resulting in an increase of the electrical resistivity and bulk density. The electronic valence of the rare- earth metal ions is most important for compound formation. In general, rare-earth metal ions are most stable when they are in cationic position, where Ce and Tb are both trivalent and tetravalent while Sm, Dy are divalent and trivalent [11] owing to their large ionic radius compared to that of Fe^{3+} ions in nano ferrites.The lattice will be distorted, generating internal stress and increasing the lattice constant. For the composition with orthorhombic second phase, the lattice constant is slightly smaller than unsubstituted ferrite and will decrease with the increase of rare-earth ion radius which suggests the existence of solubility limit for rare-earth ions[12]. Several methods are used for synthesizing nano sized spinel ferrites, such as co-precipitation, sol-gel, micro-emulsion, hydrothermal and reverse micelle[13-14].Solution combustionmethod[15], soft mechanochemical Method[16], conventional solid state method[17],Combustion Method[18], and ball milling method etc. In the present work we reported the results of synthesis and structural properties of Cu-Zn-Ce mixed nano Ferrites by non conventional citrate gel auto combustion method.

Characterization Techniques

The structural characterization of the synthesized samples with formula $Co_{0.75}Mg_{0.25}Ce_xFe_{2-x}O_4$ (where X = 0.00, 0.05, 0.10, 0.15,0.20,0.25) were carried out at room temperature by X-ray diffractometer using Cu Kα radiation (λ=1.5405Å) by scanning in the range of 10^o to $80^o$where the phase and crystallite size were. From scanning electron microscope, the synthesized nano samples surface morphology and their average particle size was analyzed.Energy Dispersive Spectrometer (EDS) was used for elemental analysis of the samples. The FTIR absorption spectra of powders (as pellets in KBr) were recorded by Fourier Transform

Infrared Spectrophotometer in the range of 200 to 4000 cm^{-1}. UV-VIS Spectroscopy was recorded in the range of 200-400nmregions.Fluorescence Spectroscopy were recorded at 200–800 nm wavelength region and excited sample at 400 nm wavelength region.

XRD for Co-Mg-Ce nano ferrites

Fig 1.1 depicts the XRD graphs of cerium co-doped Co-Mg nano ferrites. From XRD plots clearly observed that single phase cubic spinel structure. Single phase confirms from the peaks without any other impurity peaks and also confirms FD_3M space group from the XRD plots also observed that peak indexed (111), (220), (311), (222), (422), (511) &(440)[19-20]. The XRD parameters such as average crystalline size, lattice parameter, volume of unit cell and x-ray density were calculated from above mentioned formulas.

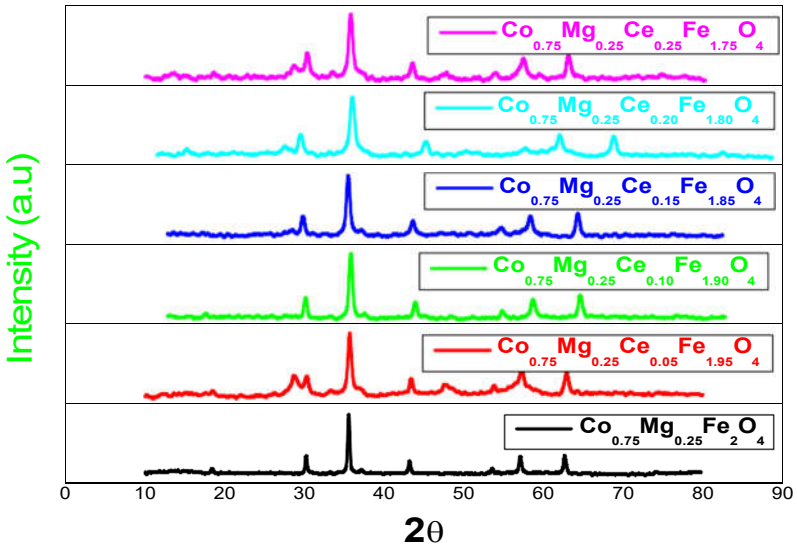

Fig 1.1XRD pattern of Co-Mg-Ce nano ferrites

Fig 1.2 shows the variation of average crystalline size and lattice parameter of the cerium co-doped Co-Mg mixed nano ferrites. From the plots clearly observed that the average crystalline size of the sample decreased with increasing cerium co-dopant concentration of the samples[21-22]. The lattice parameter was increasing with increasing the co-dopant content of cerium, it could be due to smaller ionic radius of Fe^{3+}(0.067nm), compare to Ce^{3+} (0.102nm)ionic radius.

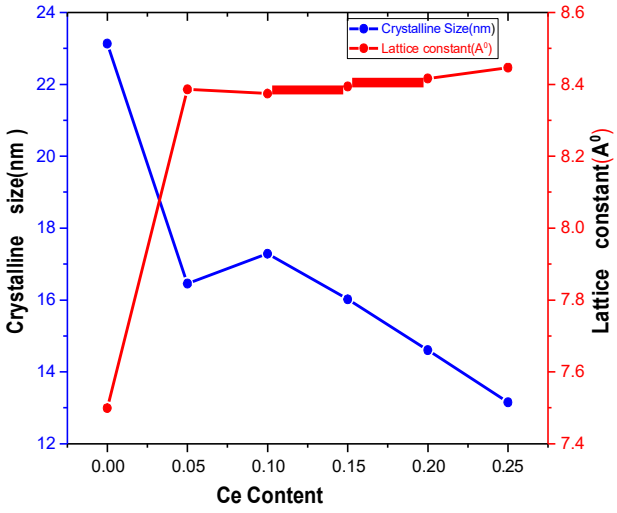

Fig 1.2 Average crystalline size variation and Lattice parameter for Sm doped Cu-Zn nanoferrites

Fig 1.3 shows the variation of volume of unit cell and x-ray density of the cerium co-doped Co-Mg mixed nano ferrites. Volume of unit cell of the samples increaseswith dopant concentration. Volume of unit cell depends on lattice parameter of the synthesized nano ferrites. X-ray density value of the pure sample high i.e. 7.113, up on increasing the dopant concentration on Fe^{3+} ions, x-ray density was decreased, later it increases constantly,x-ray density is mostly dependson molecular weight of the sample, volume of unit cell, dopant concentration and also sintering temperature[23].All these parameters such average crystalline size, lattice parameter, volume of unit celland x-ray density values were tabulated in **Table 3.2**.

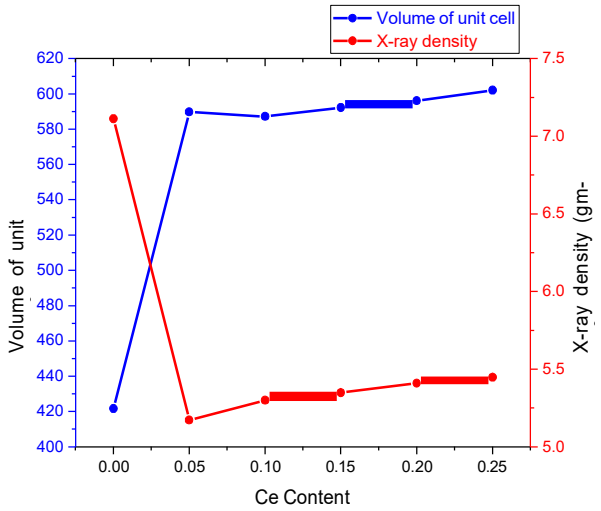

Fig 1.3 Volume of unit cell variation and X-ray density variation of Ce doped Co-MgFerrites.

Crystalline size,lattice parameter, volume of the unit cell and x-ray density for various compositions of $Co_{0.75}Mg_{0.25}Ce_xFe_{2-x}O_4$ (X=0.00-0.25)mentioned in the**table 1.1**

S.No	Composition	m.wt (gm/mol)	Crystalline Size(nm)	Lattice Constant (A°)	Volume $(A^\circ)^3$	X-ray Density gm/cc
1	$Co_{0.75}\ Mg_{0.25}Fe_2O_4$	225.962	23.13	7.499	421.706	7.113
2	$Co_{0.75}\ Mg_{0.25}\ Ce_{0.05}\ Fe_{1.95}\ O_4$	229.723	16.454	8.386	589.745	5.173
3	$Co_{0.75}\ Mg_{0.25}\ Ce_{0.10}\ Fe_{1.90}\ O_4$	234.389	17.286	8.374	587.217	5.301
4	$Co_{0.75}\ Mg_{0.25}\ Ce_{0.15}\ Fe_{1.85}\ O_4$	238.602	16.018	8.394	592.280	5.350
5	$Co_{0.75}\ Mg_{0.25}\ Ce_{0.20}\ Fe_{1.80}\ O_4$	242.816	14.601	8.416	596.097	5.410
6	$Co_{0.75}\ Mg_{0.25}\ Ce_{0.25}\ Fe_{1.75}\ O_4$	247.029	13.155	8.446	602.066	5.449

Table 1.1 Crystalline size,lattice parameter, volume of the unit cell and x-ray density for various compositions of Co-Mg-Ce mixed nano fertites.

SEM micrographs of Co-Mg-Ce nano ferrites

Fig 1.4 depicts the SEM images of Ce co-dopant Co-Mg nano ferrites. All the SEM images clearly show that agglomeration of fine nano particles. Agglomeration structures indicate

that sample particles could not be distributed uniformly[24]. All the images appeared at nano scale region.

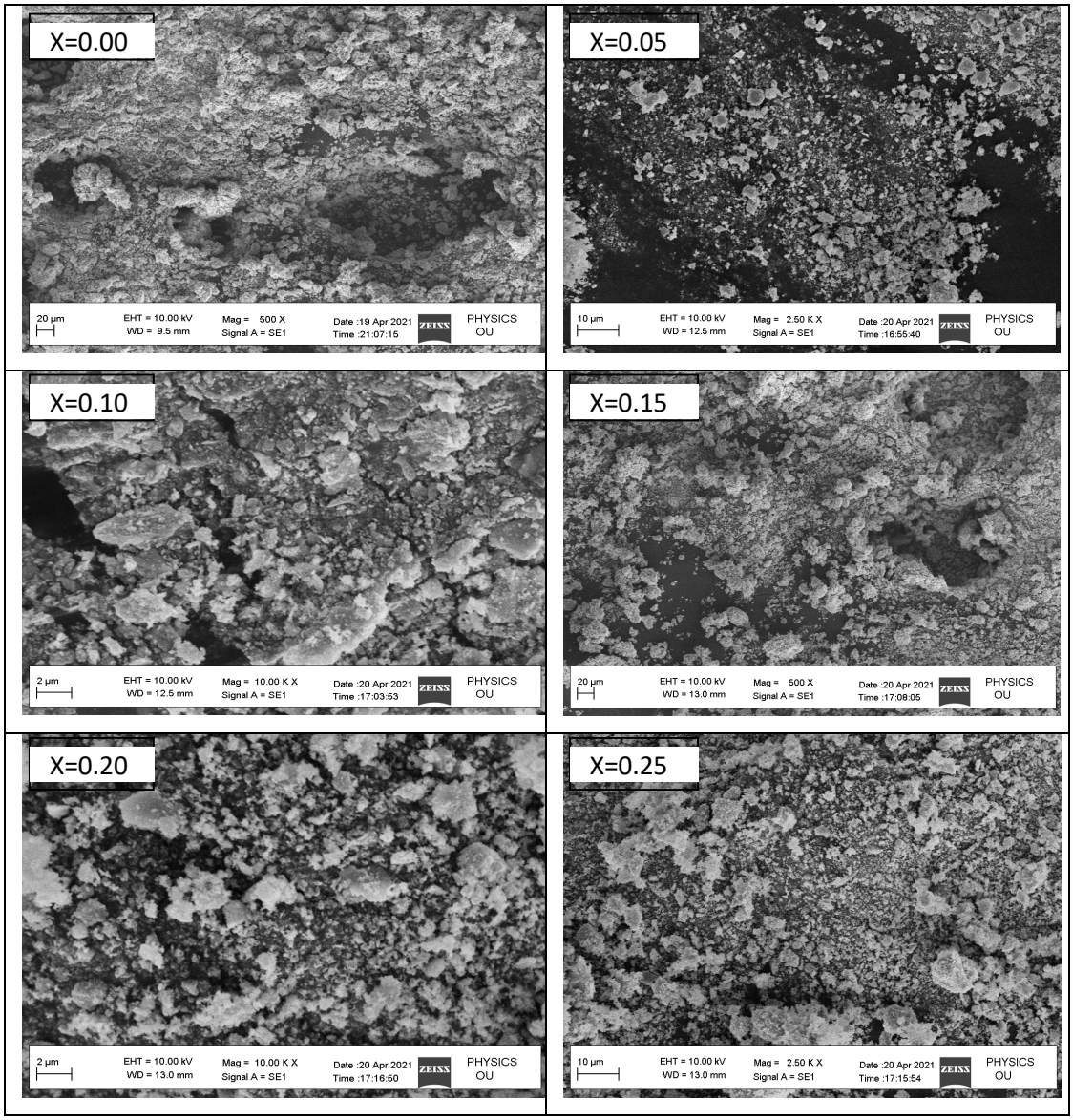

Fig 1.4SEM Micro graphs of Co-Mg-Ce mixed nano ferrites

EDS of Co-Mg-Ce nano ferrites

Fig 1.5 depicts EDAX spectral images of Ce co-dopant Co-Mg nano ferrites. EDS spectra significantly uses to know the material qualitative analysisFrom the spectral deep analysis, it is clearly observed that the samples contain all initial elements such as Co, Mg, Ce, Fe and O present in stoichiometric ratio

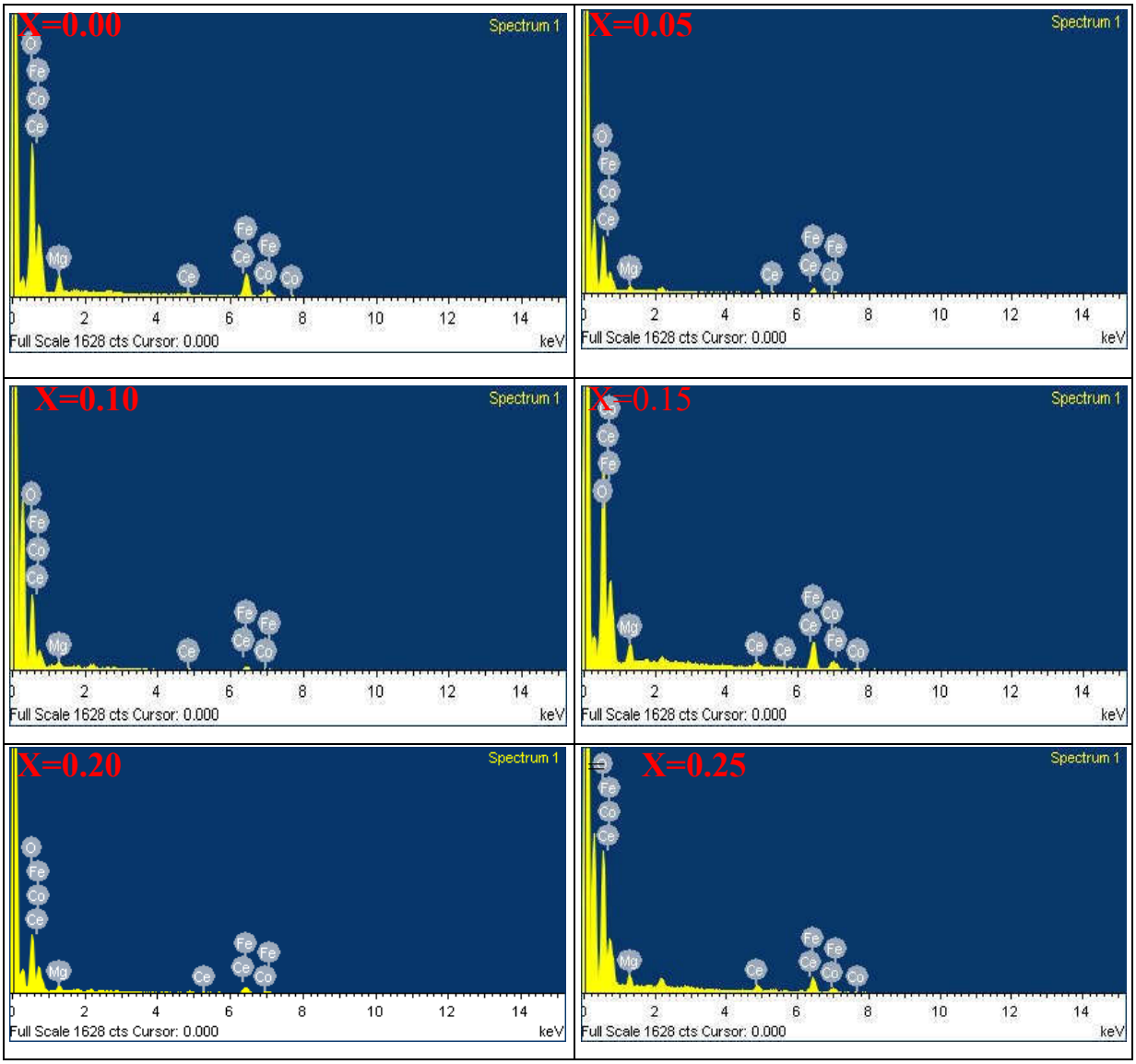

Fig1.5 EDX Graphs of Co-Mg-Ce mixed nano ferrites

Atomic % and elemental % of the above-mentioned elements such as Mg, Sm, Fe, O were tabulated in **table 1.2**

S.No	Element	O		Fe		Co		Mg		Ce	
	Ferrite Composition	Element %	Atomic %	Element %	Atomic %	Element %	Atomic %	Element %	**Atomic** %	Element %	**Atomic** %
1	$CoMgFe_2O_4$	25.43	53.73	47.98	29.03	25.08	14.38	2.20	3.06	0	0
2	$CoMgCe_{0.05}Fe_{1.95}O_4$	27.37	60.09	38.50	24.22	15.80	9.42	2.18	3.13	17.10	4.25
3	$CoMgCe_{0.10}Fe_{1.90}O_4$	35.23	66.68	34.60	18.76	22.09	11.35	1.42	1.77	6.65	1.44
4	$CoMgCe_{0.15}Fe_{1.85}O_4$	25.31	55.13	39.73	24.79	25.90	15.32	2.21	3.03	6.94	1.73
5	$CoMgCe_{0.20}Fe_{1.80}O_4$	25.24	56.14	40.59	25.87	18.34	11.38	2.25	3.29	13.09	3.33
6	$CoMgCe_{0.25}Fe_{1.75}O_4$	27.06	59.21	33.52	21.93	21.93	13.03	1.99	2.87	15.50	3.87

Table 1.2 Atomic % and elemental % of Co-Mg-Ce nano ferrites

FTIR study of Co-Mg-Ce nano ferrites

The spectral data of Co-Mg-Ce nano particles illustrates that **Fig 1.6**. FTIR spectral plots, plotted between transmittance and wave number. FTIR is significant technique to know the functional group of the material. From the spectral analysis two absorption peaks were observed that is $\nu_1$and ν_2. The ν_1 peak, which was corresponds to stretching vibrations frequency of tetrahedral (a) site that corresponds wave number region near to 590-600cm^{-1}[25-26]. Another ν_2 peak observed at 390-400 cm-1 region, which corresponds to stretchingvibrations frequency of the octahedral (b) site[27].

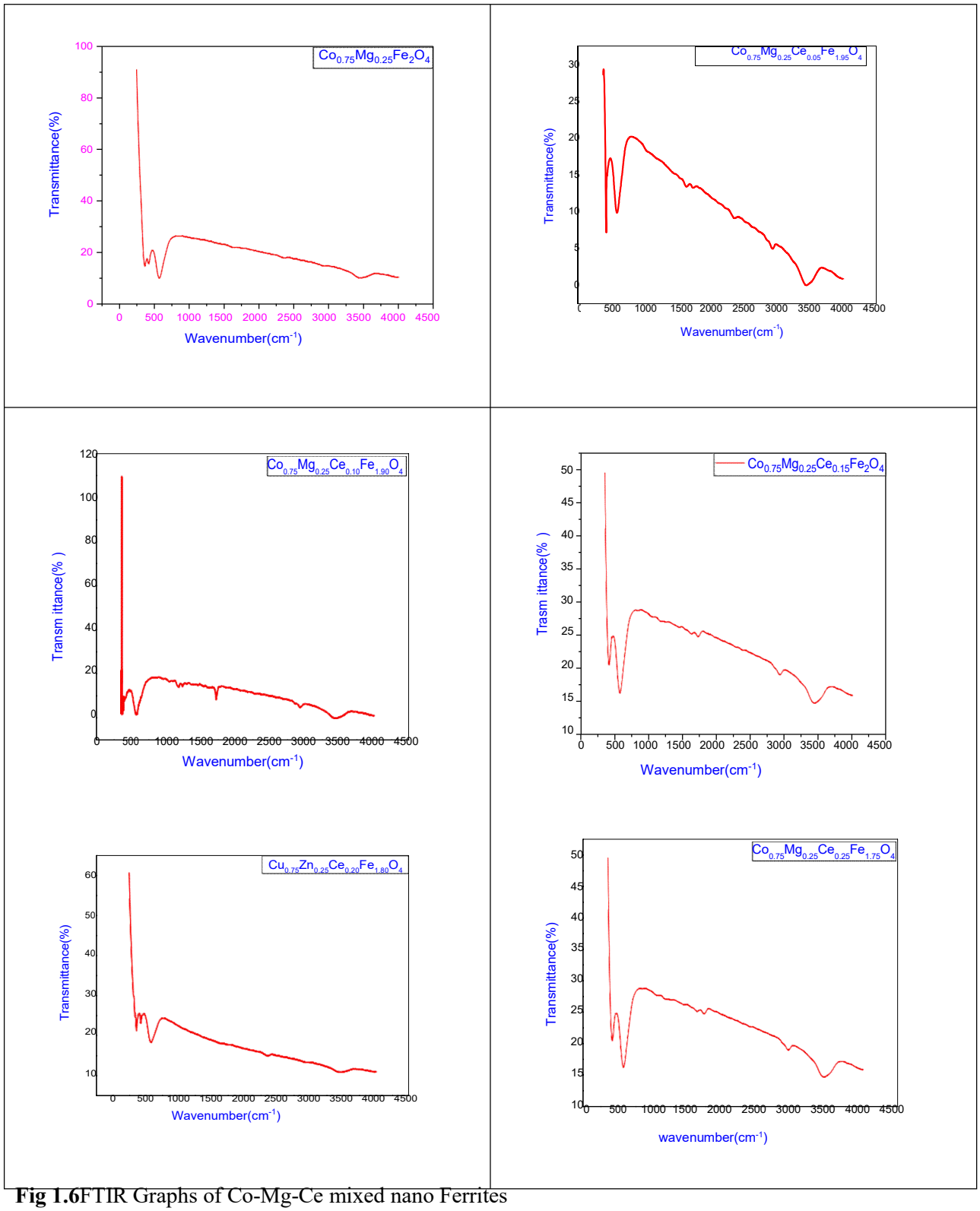

Fig 1.6FTIR Graphs of Co-Mg-Ce mixed nano Ferrites

UV-Visible spectroscopy of Co-Mg-Ce nano ferrites

Fig1.7 indicates that the UV –Vis's spectra of Co-Mg-Ce from the spectral data it shows that cut off wavelength region decreases with increasing the dopant concentration the band gap energy of the samples calculated by using above mentioned formula. The calculated band gap energy of synthesized samples was increased from 2.47 to 2.60 eV, with increasing co-dopant concentration of cerium[28-29]. The samples band gap energy values exhibit the semiconducting nature, the band gap energy variation due to higher ionic radios of Ce^{3+}(0.102 nm) compare with Fe^{3+} (0.067 nm) ionic radios and also depends upon method of synthesis, crystalline size and sintering temperature[30].

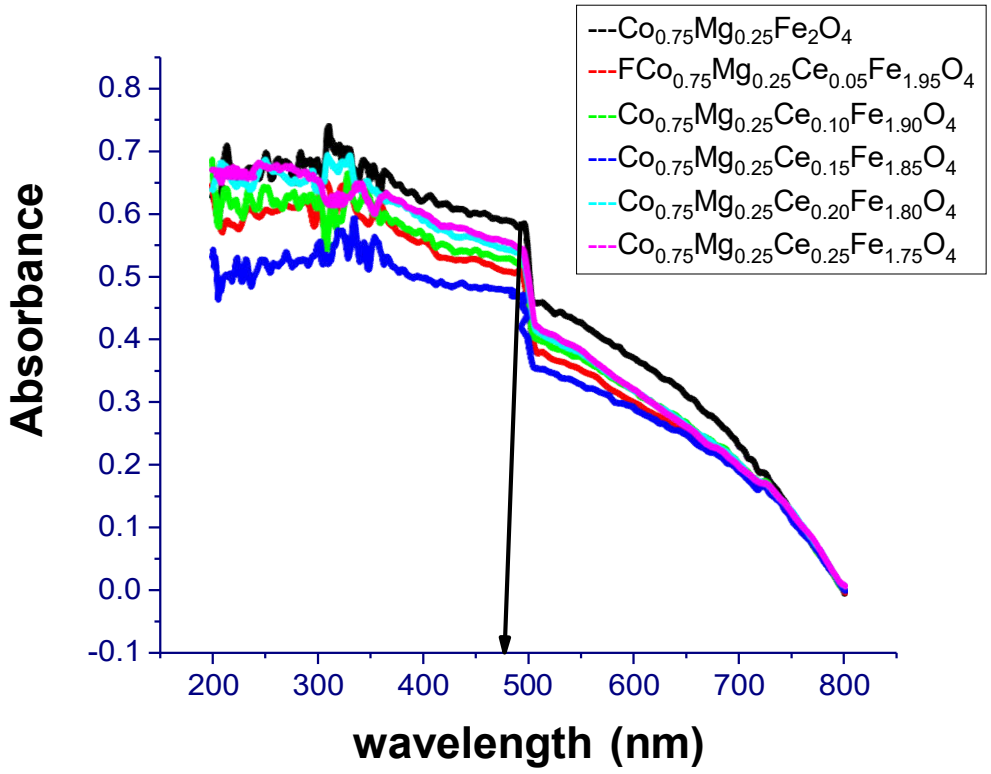

Fig 1.7 UV–Vis plots of Co-Mg-Ce nano ferrite

Table 1.3: Cut off wavelength and band gap energy of $Co_{0.75}Mg_{0.25}Ce_xFe_{2-x}O_4$

S.NO	Composition	Cut Off Wavelength (nm)	Band gap Energy (ev)
1	$Co_{0.75}\ Mg_{0.25}Fe_2O_4$	502	2.47
2	$Co_{0.75}\ Mg_{0.25}\ Ce_{0.05}\ Fe_{1.95}\ O_4$	497	2.49
3	$Co_{0.75}\ Mg_{0.25}\ Ce_{0.10}\ Fe_{1.90}\ O_4$	496	2.50
4	$Co_{0.75}\ Mg_{0.25}\ Ce_{0.15}\ Fe_{1.85}\ O_4$	487	2.54
5	$Co_{0.75}\ Mg_{0.25}\ Ce_{0.20}\ Fe_{1.80}\ O_4$	484	2.56
6	$Co_{0.75}\ Mg_{0.25}\ Ce_{0.25}\ Fe_{1.75}\ O_4$	476	2.60

Conclusions:

- From citrate gel auto combustion method $Co_{0.75}Mg_{0.25}\ Ce_xFe_{2-x}O_4$ (where X = 0.00, 0.05, 0.10, 0.15,0.20,&0.25) mixed nano ferrites were synthesized successfully.
- XRD pattern reveals that single phase cubic spinel structure without any other impurities peaks and confirms FD_3M space group.
- Synthesized samples lattice parameter varies, could suggest that obeys Vegard's law.
- SEM images revels that agglomeration present in all the samples which conforms particles could not equally distributed.
- From EDS graphs it is clear that the according to stoichiometric ratio elements are present without any other impurities.
- FTIR spectra revels that the information about the stretching vibrations of tetrahedral and octahedral sites (600-400 cm-1).
- Band gap energy of the synthesized samples from 2.4 to 2.55 eV, it indicates samples behaves semiconductor.

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