STRUCTURAL AND MORPHOLOGICAL CHARACTERIZATION OF MIXED SPINEL NANO-FERRITES AND CA-W NANO HEXAFERRITES.

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A B S T R A C T

Nanoparticles of mixed spinel ferrite having generic formula of $(NiZn)xCu_{1-2x}Fe_2O_4$ and hexagonal Ca-W ferrite of formula $Ca_2Co_{2-x}Ni_xFe_{16}O_{27}$ were respectively prepared by sol gel auto combustion method and co-precipitation method. The prepared samples were annealed for 4 hrs at 800^oC to obtain the pure phase of Ni-Zn spinel ferrite and W-type Hexagonal ferrite. The X-ray diffraction confirmed the typical soft ferrite structure in spinel and magnetoplumbite hard ferrite structure formation of the ferrites with a single phase. The morphological characterization was done by using scanning (SEM) and transmission electron microscopy (TEM) respectively. The SEM reveals the randomly oriented cubic shape particles for spinel ferrite and a plate- like hexagonal structure for Ca-W ferrite. TEM counter-verified the cubic shape and further confirms that prepared sample lies within the nano meter scale. The Ca-W ferrite was studied for concentrations (x= 0, 1 and 2) for the effects of Ni^{2+} cationic substitution for Co^{2+} on the structural properties.

Keywords: Spinel ferrites, Hexa ferrites, auto combustion, co-precipitation, X-ray diffraction, SEM and TEM.

1. INTRODUCTION

The ferrites are the magnetic materials exhibiting properties which are commercially used for magnetic storage, microwave absorption and permanent magnets. The different types of ferrites include spinel type, garnet type and hexagonal ferrites. The ferrites with cubic structure known spinel ferrites are extensively attractive only because of its good performance and broad range of applications but there are also a group of ferrites with a hexagonal crystal structure, also known as hexaferrites.[1]Hexaferrites have a hexagonal crystal structure. The existing six types of hexaferrite structures are designated as: M, Y, Z, W, X and U. The general formulation of hexaferrites is MxMez(Fe2O3)y, the ratios of x/y for M, Y, Z, W, X and U are 1:6, 1:3, 1:4, 1:8, 1:7 and 2:9, respectively [2-4]. M in the chemical formula of hexaferrites represents the ions of Ba, Sr, Pb, Ca, La, and Me is usually transition element (Zn, Mn, Co, etc.). As is the same in the spinel structures, the substitution of Fe^{3+} ions can be other trivalent cations such as Al^{3+}, Cr^{3+}, etc.The Ni-Zn nanoparticles ferrite has a unique chemical and structural behaviour that makes it the prolific material in many medical and technological applications such as magnetic delivery of drugs, ferrofluids, MRI, recording media etc. The size of spinel ferrite if confined below 25 nm then the exceptional property called as superparamagnetism occurs that offers outstanding opportunities in manipulation of nanoparticles to enhance the various applications. Numerous synthesized methods are available to prepare the spinel ferrites viz. sol-gel auto combustion, co-precipitation, hydrothermal, solid state, miscelles, microemulsion etc. The present research work aimed to prepare the Ni-Zn mixed ferrites via two different chemical routes to understand how different synthesis methods

influence the structural and morphology properties. The Ca-W ferrite was studied for concentrations (x= 0, 1 and 2) for the effects of Ni^{2+} cationic substitution for Co^{2+} on the structural properties.

2. EXPERIMENTAL

The chemically AR grade precursor nitrates were used as starting materials and urea [NH_2-CO-NH_2] used as a fuel. The lone sample of $(NiZn)_xCu_{1-2x}Fe_2O_4$ for x = 0.3 was synthesized by two most generous techniques viz. sol-gel auto combustion route and co-precipitation method. $Ca_2Co_{2-x}Ni_xFe_{16}O_{27}$ was prepared by sol gel auto combustion method and studied for concentrations (x=0, 1 and 2).

Sol Gel Auto Combustion Technique

The metal nitrates were dissolved in minimum amount of distilled water. Urea was used as fuel and dissolved into the solution to give a molar ratio of metal ions to urea of 1:1 to form the sol. Then the sol was put on a magnetic hot plate and heated at 70^0C to obtain viscous gel. The as obtained gel was exposed to the specially designed microwave oven, followed by an instantaneous gel ignition with the formation of large amount of gas. The resulting precursor' powder was calcined at 800^0C for 4 hrs and grinded for 2 hrs to obtain pure phase of mixed ferrite [5]. The synthesized ferrites were kept in crucible and sintered at 800^0C for 4 hours by slowly raising the temperature of the furnace at the rate of 100^0C per hour. After sintering the furnace was cooled at the same rate. Then powdered samples were further grinded to fine powder. Finally, the powder so formed was pelletized and then heated for 4 hrs at constant temperature of $800°C$ in an electric furnace to remove any residual organic material present so as to obtain single-phase ferrites.

Co precipitation Technique

The stoichiometric proportion of precursor were dissolved in deionzied water that include the slow addition of sodium hydroxide (1M) solution to form ferrite precipitate at room temperature. The aqueous solution put on the magnetic stirrer and stirred at 600 rpm for 30 mins to obtain better homogeneity. The dark brown precipitates as obtained filtered, washed off with distilled water and dried overnight. The precipitated was calcinated at 800^oC and grinded for 2 hrs to have ultrafine particles [6, 7].

Pellet formation

The sintered pellets were grinded in agate mortar and little binder such as polyvinyl alcohol is added to it and then crushed to have a fine powder. The powder was poured in to a punch of die of about 13 mm diameter and pressed in a hydraulic press with a presser of about 25 Kilo-tones for about 15-20 minutes. After removing the load, the pellets were taken out from die. The pelletized samples were finally sintered at 400^0C for 3h and slowly cooled to remove the binder. The sintered specimens were used for further characterization.

3. CHARACTERIZATION TECHNIQUE

he structural characterization of samples has been studied by X- ray diffraction (Bruker Advance X-ray diffractometer). The scanning electron microscopy (SEM-JSM-7600F) and transmission electron microscopy (TEM-CM200) were used to characterize the nanostructure features of the samples.

4. RESULT AND DISCUSSION

The synthesized ferrites were analyzed with the X-ray diffraction technique to check the structural details. Figure 1 shows the XRD patterns of spinel ferrite sample synthesized by sol- gel auto combustion and co-precipitation method. The peaks being there (1 1 1), (3 1 1), (2 2 2), (4 4 0) in the XRD clearly indicate the formation of single phase spinel ferrite structure. The XRD pattern was compared with and indexed using ICDD card no. 86-2287 that confirms the space group fd-3m [8]. The figure show XRD peaks are little broad reveals the smaller grain size within the 100 nm. Generally sol-gel and co-precipitation technique yields the nano particles of ferrites [9, 10].
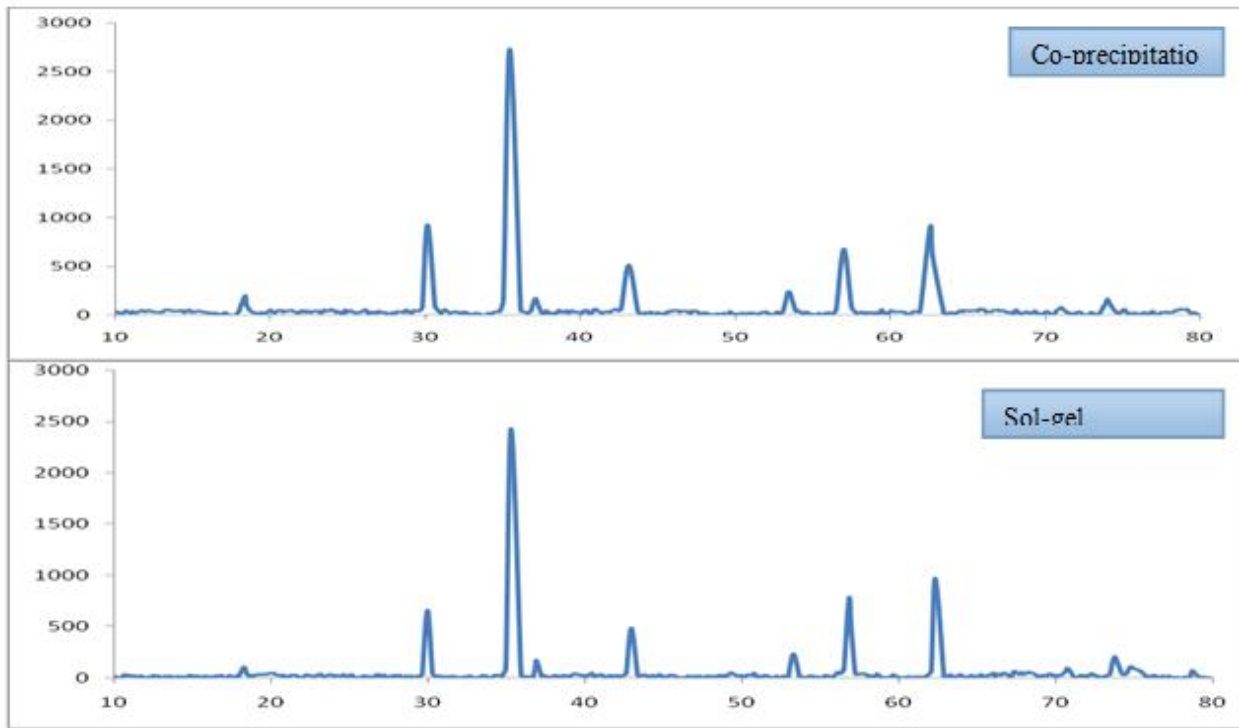
Figure 1: X-ray diffraction pattern of $(NiZn)_xCu_{1-2x}Fe_2O_4$ (x = 0.3)

The particle size obtained using De-bye scherrer formula was just about 54 nm and 37 nm for sol-gel and precipitation method respectively.

The lattice constant & average particle size are depicted in the table no. 1.

Table No. 1: The values of structural parameters calculated from XRD of $(NiZn)_{0.3}Cu_{0.4}Fe_2O_4$

Sr.No.	Method	Lattice parameter (Å)	Particle Size (nm)	Porosity (%)
1	Co-precipitation	8.356	37	40
2	Sol-gel combustion	8.510	54	48

The XRD pattern of $Ca_2Co_{2-x}Ni_xFe_{16}O_{27}$ (x = 0, 1, 2) powders sintered at 800^0C was shown in Fig. 2-4. All diffraction features have been indexed to space group P63/mmc (published pattern: ICDD-#78-0135), corresponding to a hexagonal crystal structure.
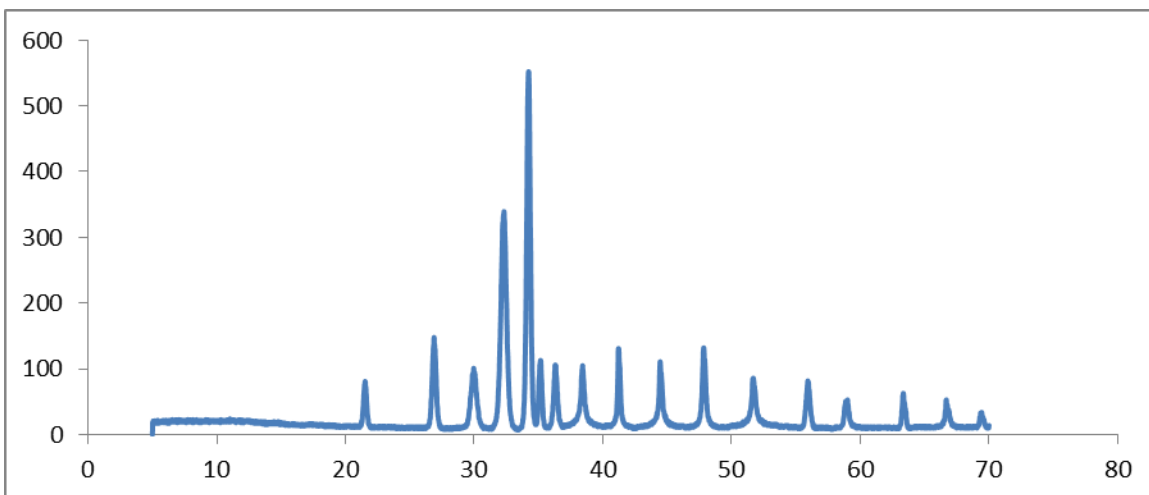

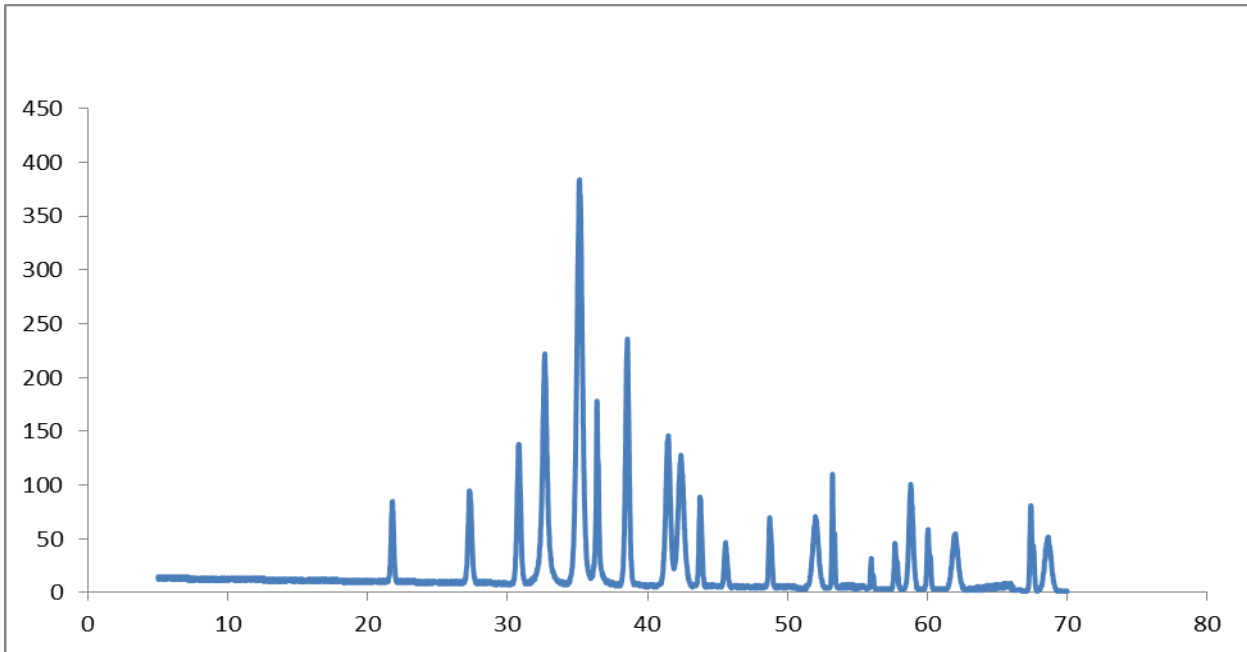**Fig.2: X-ray diffraction patterns of the system $Ca_2Co_{2-x}Ni_xFe_{16}O_{27}$ (x= 0)**

Fig.3: X-ray diffraction patterns of the system $Ca_2Co_{2-x}Ni_xFe_{16}O_{27}$ (x= 1)
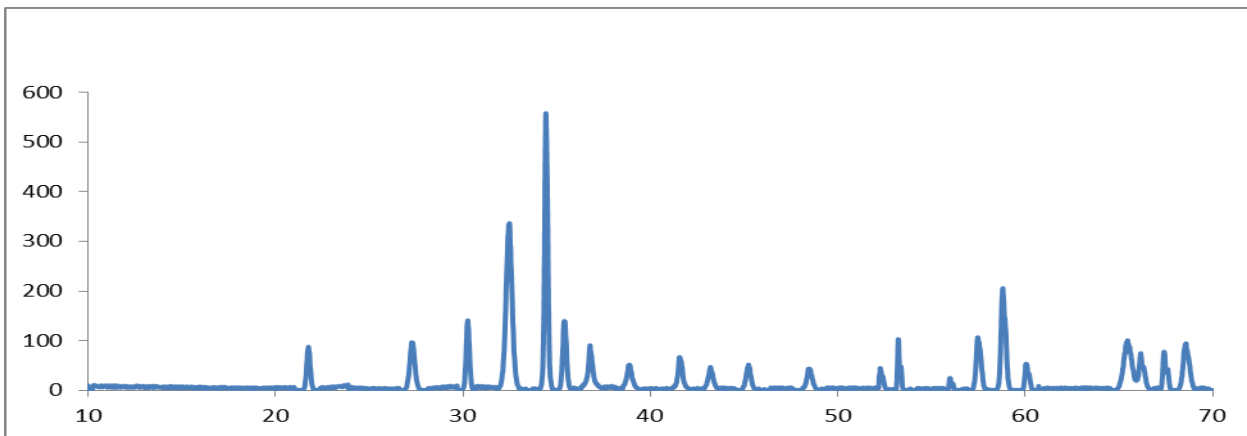
Fig.4: X-ray diffraction patterns of the system $Ca_2Co_{2-x}Ni_xFe_{16}O_{27}$ (x= 2)

The X-ray density (ρx) increased linearly with increasing x, as shown in Table 2. This increase is mainly due to the increase of the molecular weight of the W-type hexaferrite when Co replaced Ni completely.

Table 2: X-ray Diffraction Calculations for $Ca_2Co_{2-x}Ni_xFe_{16}O_{27}$

Concentration	Lattice constant		$V=a^2c$ ($Å)^3$	dx (gm/cm^3)	d_b (gm/cm^3)	Porosity (%)	D (nm)
	a(Å)	c (Å)					
x=0	5.96	32.87	1167.6	4.333	2.03	46	23.19
x=1	5.78	32.8	1095.79	4.616	2.03	44	27.68
x=2	5.7	32.7	1062.42	4.7605	2.03	43	48.94

SCANNING ELECTRON MICROSCOPY
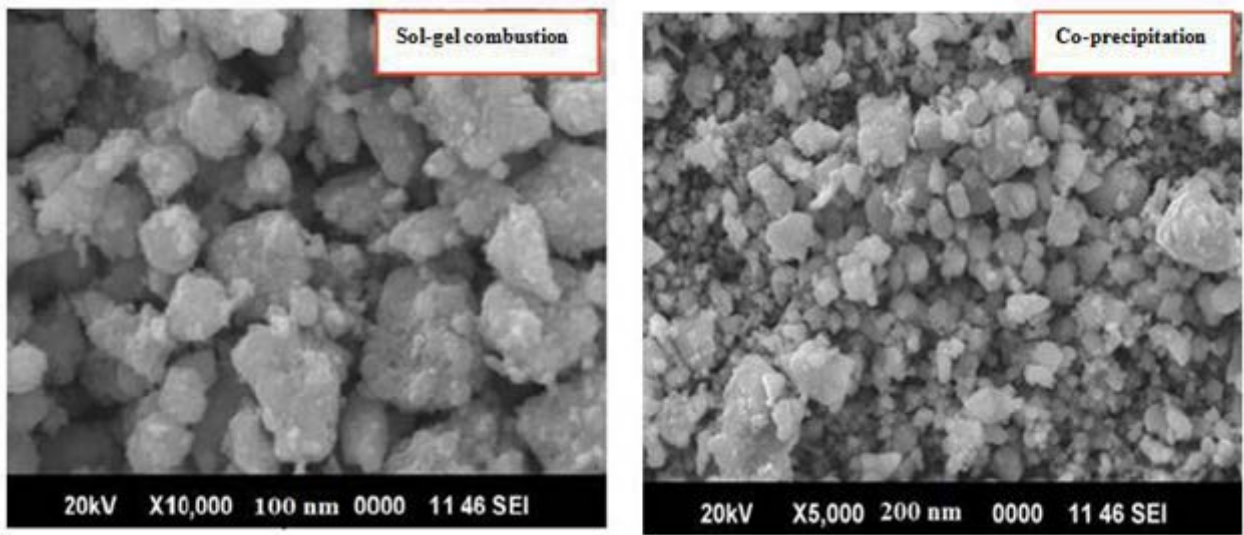
Figure 5: SEM images of (NiZn)xCu1-2xFe2O4 (x = 0.3)

Figure5 shows the SEM micrographs of prepared sample. Apparently the SEM image indicates the structural changes with respective synthesis method. The morphology looks non-uniform with agglomeration and grain size is somewhat affected by the respective synthesis method. Comparatively sol-gel method shows large voids indicating more porous nature of sample and is expected as large amount of gases are coming out during the synthesis.
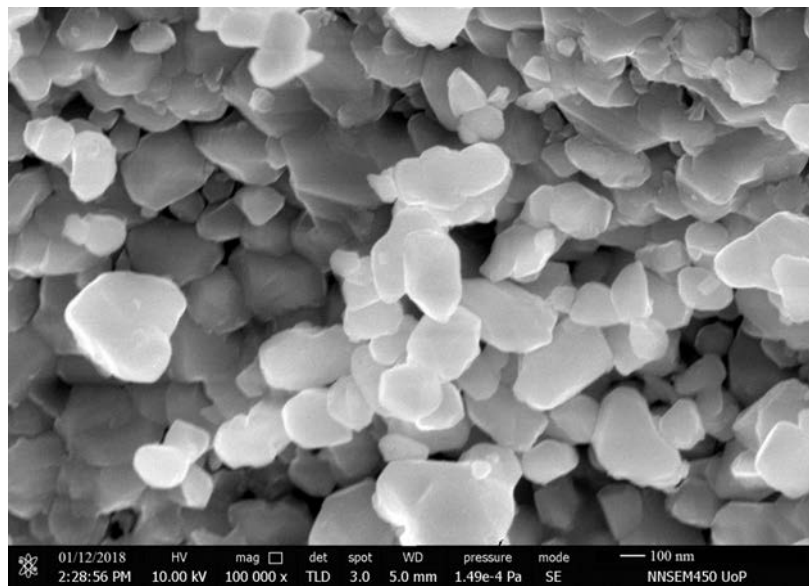

Fig.6: SEM micrograph of $Ca_2CoNiFe_{16}O_{27}$ for x=1.

Representative SEM images of $Ca_2Co_{2-x}Ni_xFe_{16}O_{27}$ for x = 1 sintered at 800° C (Fig. 6) revealed granular structure mainly composed of regular hexagonal plates characterized by a wider distribution of particle size. The diameters of the hexagonal plates ranged between 30-50 nm with average grain size of 40 nm. Since the critical single-domain size in hexaferrite was reported to be 30 nm [11], we may conclude that the sample consists of multi-domain particles. The particles in this sample stacked closely with relatively low porosity.
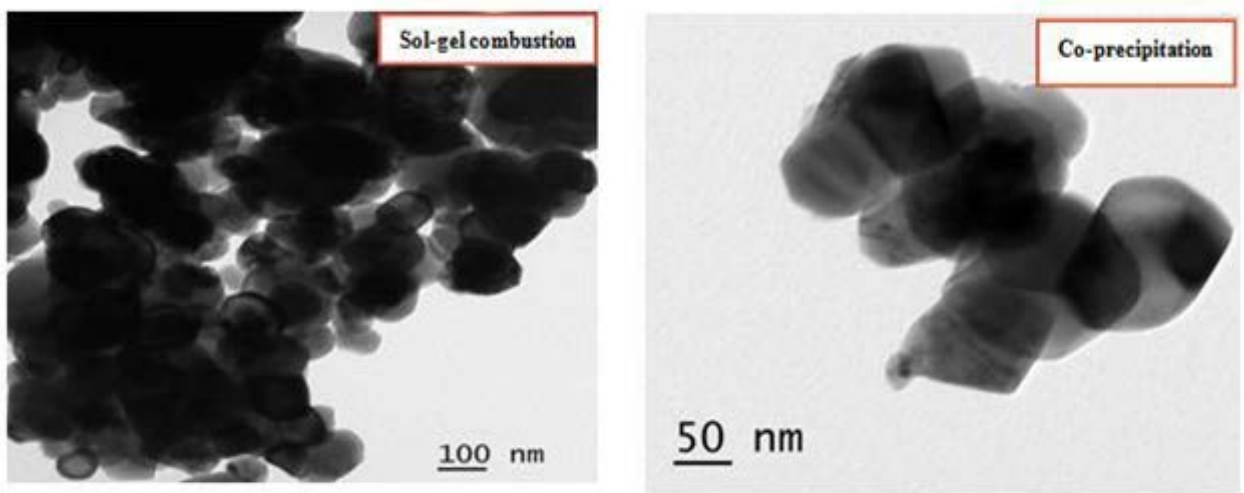
Fig 7: TEM images of $(NiZn)_x Cu_{1-2x} Fe_2 O_4$ (x = 0.3)

Figure 7 shows the TEM micrographs of prepared mixed spinel ferrites by sol gel combustion and co-precipitation method respectively. TEM shows cubic morphology of synthesized ferrite with sharp edges. The grain size obtained from TEM shows good agreement with the average particle size calculated from scherrer formula. The TEM micrograph of prepared sample by sol-gel combustion method shows the agglomeration that resemblance with respective SEM image.

CONCLUSION

Nano-spinel ferrites and nano Ca-W hexaferrites are successfully synthesis by co-precipitation and sol-gel auto combustion techniques.Both XRD indicates crystalline nature and formation of cubic structure of synthesis material & values of lattice parameters being supported it.There was no extra lines were detected hence confirm the single magnetoplumbite phase in the reported samples.The SEM shows the irregular morphology with large voids indicating porous material for spinel structure and a plate- like hexagonal structure for Ca-W ferrite. The SEM micrograph of the doped samples exhibits a steady grain growth and the samples appear to be mixture of homogenous individual particles.TEM shows cubic structure of spinel ferrites with particle size in nano meter range. With sol-gel auto combustion route, Ni and Co substituted calcium hexaferrites nano particles have been effectively and successfully synthesized. The Ni-Zn Spinel ferrite synthesized by sol-gel combustion method showed increased porosity, particle size and lattice parameters as compared to the samples synthesized by Co-precipitation method.

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