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# Magnetic Properties of Nanocrystalline ε-Fe<sub>3</sub>N and Co<sub>4</sub>N Phases Synthesized by Newer Precursor Route

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#### Abstract

Nanocrystalline  $\varepsilon$ -Fe<sub>3</sub>N and Co<sub>4</sub>N nitride phases are synthesized first time by using tris(1,2-diaminoethane)iron(II) Chloride and tris(1,2-diaminoethane)cobalt(III) Chloride precursors, respectively. To prepare  $\varepsilon$ -Fe<sub>3</sub>N and Co<sub>4</sub>N nitride phases, the synthesized precursors were mixed with urea in 1:12 ratio and heat treated at various temperatures in the range of 450 to 900 <sup>o</sup>C under the ultrapure nitrogen gas atmosphere. The precursors are confirmed by FT-IR study. The  $\varepsilon$ -Fe<sub>3</sub>N phase crystallizes in hexagonal structure with unit cell parameters, a=4.76 Å and c=4.41 Å. The Co<sub>4</sub>N phase crystallizes in face centred cubic (fcc) structure with unit cell parameters, a=3.55 Å. The estimated crystallite size for  $\varepsilon$ -Fe<sub>3</sub>N and Co<sub>4</sub>N phases are 29 nm and 22 nm, respectively. The scanning electron microscopy (SEM) studies confirm the nanocrystalline nature of the materials. The values of saturation magnetization for  $\varepsilon$ -Fe<sub>3</sub>N and Co<sub>4</sub>N phases are found to be 28.1 emu/g and 123.6 emu/g, respectively. The reduction of magnetic moments in ultrafine materials compared to bulk materials have been explained by spin pairing effect, lattice expansion, superparamagnetic behaviour and canted spin structures at the surface of the particles.

**KEYWORDS:** A. nitrides, B. magnetic materials, C. chemical synthesis, D. x-ray diffraction, E. crystal structure.

#### 1. Introduction

The materials at nanometer scales are very important for their applications in catalysis, magnetic recording, magnetic refrigeration, ferrofluids, structural materials and permanent magnetic materials etc. [1-5]. The properties of nanostructures depend on shape and size distributions. In order to synthesize the nanoparticle with proper shape and size distribution, chemical synthesis plays an important role [2]. The chemical synthesis involves blending of metal ions in atomic state and favours facile reactions. Various reports are found on the synthesis of  $\varepsilon$ -Fe<sub>3</sub>N and Co<sub>4</sub>N phases [2,6-10]. In most of the reports metal nitrides are generally produced by nitridation of metal, metal halides, metal oxides and organometallic precursors at high temperatures. Depending upon the nature of the precursor and nitridation conditions, one can get various nanocrystalline  $\varepsilon$ -Fe<sub>3</sub>N and Co<sub>4</sub>N nitride phases with tunable shape and size distributions [2,11]. However, there are synthetic difficulties in synthesizing these materials using ammonia gas as a vector. The synthetic difficulties involve, (1) it is difficult to control the nitrogen content in the nitride materials (2) sufficient amorphous fractions are present and (3) side reactions may occur.

Nitridation of iron containing precursors produce varieties of phases:  $\alpha$ ,  $\gamma$ ,  $\gamma'$ ,  $\varepsilon$ ,  $\xi$ ,  $\alpha'$ and  $\alpha''$ . The  $\varepsilon$ -Fe<sub>3</sub>N phase has extended region in the phase diagram depending upon nitrogen content [12]. The  $\varepsilon$ -Fe<sub>3</sub>N phase crystallizes in hexagonal structures and shows attractive magnetic properties. Similarly nitridation of cobalt containing precursors lead to various phases such as Co<sub>2</sub>N, Co<sub>3</sub>N and Co<sub>4</sub>N etc. The Co<sub>4</sub>N phase crystallizes in fcc cubic crystal structure and possesses high value of saturation magnetization [11]. The crystallography and magnetic properties of these nanomaterials are sensitive to nitrogen content and ultrafine nature of the materials. Therefore, research on this topic merits further investigations.

Recently, literatures are available for the preparation of nitrides and carbides materials by using an urea route [13,14]. In this route, various stoichiometric amounts of urea and metal precursors were loaded and fired at nitrogen atmosphere at various temperatures. It is to be noted that depending upon the metal: urea ratio, the nitride or carbide formation takes place. The synthesized products are nanocrystalline with high surface area [15]. The precursors play an important role in the synthesis of these materials. In the literature, scanty knowledge is available regarding development of newer synthetic routes for E-Fe<sub>3</sub>N and Co<sub>4</sub>N nitride phases. Therefore, this study investigates the synthesis of ε-Fe<sub>3</sub>N phase and Co<sub>4</sub>N nitride materials by using urea route. Various precursors are used for the synthesis of nitride and carbide by urea route such as metal oxide and metal chloride etc. [14,16]. In this study, we prepared tris(1,2-diaminoethane)iron(II) Chloride and tris(1,2diaminoethane)cobalt(III) Chloride and are used as metal precursors for synthesis of iron and cobalt nitrides. The presence of metal-nitrogen bonds in the precursor may facilitate the metal nitride formation by using the urea route. As far as development in this field is concerned, the current manuscript is the first time report describing the preparation of  $\varepsilon$ -Fe<sub>3</sub>N and Co<sub>4</sub>N nitride material phases using urea route.

#### 2. Experimental

#### 2.1 Precursor synthesis

#### 2.1.1 Synthesis of Iron-1,2-diaminoethane complex

This study focuses on synthesis of Iron-1,2-diaminoethane complex by literature reported method [17]. In summary, iron(III) chloride hexahydrate (4.83g, Molychem, India) was dissolved in 10 mL of distilled water and 30 mL of ethanol in a beaker. Next,

3.6 mL of 1,2-diaminoethane (Qualigens, India) was added slowly into the beaker kept in the ice bath with constant stirring. Immediately, the brown colour precipitate of tris(1,2-diaminoethane)iron(II) Chloride was obtained. The precipitate was filtered, washed with ethanol and dried at 100  $^{0}$ C in air oven for 2h. The as dried powder was used as precursor for iron metal source.

#### 2.1.2 Synthesis of Cobalt-1,2-diaminoethane complex

The cobalt-1,2-diaminoethane complex was synthesized by using literature reported method [18]. In brief, cobalt(II) chloride hexahydrate (3.9g ,Molychem, India) was dissolved in 10 mL of distilled water and 30mL of ethanol in a beaker. Next, 3.3mL of 1,2-diaminoethane (Qualigens, India) was added slowly into the beaker kept in the ice bath with constant stirring. After 15 minutes, 4 mL of 6 N HCl was added followed by addition of 3 mL of H<sub>2</sub>O<sub>2</sub>. The Yellow-orange colour precipitate of tris(1,2-diaminoethane)cobalt(III) Chloride was obtained. The precipitate was filtered, washed with ethanol and dried at 100  $^{\circ}$ C in air oven for 2 h. The as dried powder was used as precursor for cobalt metal source.

#### 2.2 Nitridation of the precursors

The precursors i.e. tris(1,2-diaminoethane)iron(II) Chloride and tris(1,2-diaminoethane)cobalt(III) Chloride were mixed with urea as nitrogen source in different molar ratios such as 1:6, 1:12 etc. 1 g of the resulting mixture was placed in an alumina boat, which was placed inside the furnace and heated under  $N_2$  (g) flow at various temperatures (450 - 900  $^{0}$ C) and time durations (3-4 h). The heating ramp was 5 K/min and the furnace was cooled naturally after the reaction.

#### 2.3 Instrumental Characterization

FT-IR spectra were recorded with a wave number ranging from 4000-350 cm<sup>-1</sup> for the tris(1,2-diaminoethane)iron(II) Chloride and tris(1,2-diaminoethane)cobalt(III) Chloride complex using an FT-IR (model: JASCO 460 plus ) instrument. The materials were mixed with solid KBr and pelletized. The X-ray diffraction (XRD) patterns were recorded using a powder X-Ray diffractometer (model: Mini Flex II, Japan) using Cu K<sub>a</sub> radiation ( $\lambda$ =0.154 nm) at a scan speed of 3°/min. The phase purity was ascertained using X-ray diffraction. Crystallite size was analyzed using Scherrer equation, t = 0.9 $\lambda$ /BCos $\theta$ , where t is the crystallite size,  $\lambda$  is the wavelength of x-ray radiation, B is the FWHM in radian and  $\theta$  is the diffraction angle [19]. The shape and morphology of the products were examined by scanning electron microscopy (SEM) (model: JEOL, JSM-6390). The magnetization measurements were carried out on solid powder material using vibrating sample magnetometer (model: ADE VSM- EV9) that can provide a magnetic field up to 20 kOe.

#### 3. Results and Discussions

#### 3.1 Precursor Characterization

The synthesized precursors tris(1,2-diaminoethane)iron(II) Chloride ( $[Fe(en)_3]Cl_2$ ) and tris(1,2-diaminoethane)cobalt(III) Chloride ( $[Co(en)_3]Cl_3$ ) have been identified by FT-IR analysis and were compared with the literature reported values [20, 21]. The FT-IR spectra of tris(1,2-diaminoethane)iron(II) Chloride and tris(1,2-diaminoethane)cobalt(III) Chloride have been presented in fig 1 and 2 respectively. The major frequencies (cm<sup>-1</sup>) and assignment for the complexes have been summarized in table no 1. The strong bands of tris(1,2-diaminoethane)iron(II) Chloride and tris(1,2-diaminoethane)cobalt(III)

Chloride at 3351 cm<sup>-1</sup> and 3510-3440 cm<sup>-1</sup> are attributed to N-H stretching vibrations of NH<sub>2</sub> group in the precursor complex. The peaks at 3006 cm<sup>-1</sup> and 3205-3090 cm<sup>-1</sup> for  $[Fe(en)_3]Cl_2$  and  $[Co(en)_3]Cl_3$  are due to C-H stretching vibrations of CH<sub>2</sub> group of diamine ligands. The C-N vibration band appears at 1033 cm<sup>-1</sup> and 1058 cm<sup>-1</sup> for iron and cobalt complexes, respectively. The NH<sub>2</sub> stretching frequencies (3412 cm<sup>-1</sup>) of the complexes are shifted compared to the pure ethylenediamine ligands. The shifting is due to the coordination of the stronger M-N bonds in the complexes [22]. In the present study, the N-H and C-H stretching frequencies of  $[Fe(en)_3]Cl_2$  and  $[Co(en)_3]Cl_3$  are broader due to the hydrated nature of complex.

#### 3.2 Solid state reactivity and XRD studies

The indexed powder XRD patterns of  $\varepsilon$ -Fe<sub>3</sub>N and Co<sub>4</sub>N phases, synthesized by using metal precursor: urea in the molar ratio of 1:12 is shown in fig 3. The iron and cobalt precursors were mixed with urea in the ratio of 1:12 and heat treated at different temperature ranging from 450 to 900 <sup>o</sup>C under the N<sub>2</sub> (g) atmosphere for 3-4 h. Experiments were done in order to get various iron nitride phases i.e. FeN,  $\varepsilon$ -Fe<sub>3</sub>N, Fe<sub>4</sub>N and Fe<sub>16</sub>N<sub>2</sub> etc. However, in the present study one could prepare only pure  $\varepsilon$ -Fe<sub>3</sub>N phase at 550 <sup>o</sup>C. It has been tried to reduce the metal precursor: urea ratios from 1:12 to 1:8 but could not succeed in preparing low nitrogen containing phases and the XRD pattern shows Fe<sub>3</sub>O<sub>4</sub> as major product. In a similar way experiments were done to get various cobalt nitride phases i.e. CoN, Co<sub>3</sub>N and Co<sub>4</sub>N etc. by applying different nitridation conditions. However, one could succeed in synthesizing pure Co<sub>4</sub>N phase at the temperature of 800 <sup>o</sup>C

In the crystal structure of  $\varepsilon$ -Fe<sub>3</sub>N phase, Fe atoms form hexagonal close packing (hcp) arrangement and N atoms occupy octahedral interstitial sites. It has been seen that long range N ordering is found in  $\varepsilon$ -Fe<sub>3</sub>N material [23]. Therefore, an enlarged unit cell with lattice parameters, a=3<sup>1/2</sup> a<sub>hcp</sub> and c=c<sub>hcp</sub>, have been considered, where hcp refers to the unit cell of hcp arrangement of iron atoms. In the present study,  $\varepsilon$ -Fe<sub>3</sub>N phase crystallizes in hexagonal structures with lattice parameters, a=4.76 Å and c=4.41 Å. The lattice parameters are larger than the literature reported values i.e. a=4.70 Å and c=4.38 Å for  $\varepsilon$ -Fe<sub>3</sub>N nitride [23, 24]. This result indicates that nitrogen content in the nitride materials exceeds the stoichiometric values of 3:1 in  $\varepsilon$ -Fe<sub>3</sub>N and could be assigned correctly as  $\varepsilon$ -Fe<sub>3</sub>N<sub>1.33</sub> [23]. The space group symmetry adopted for  $\varepsilon$ -Fe<sub>3</sub>N is P6<sub>3</sub>22 [25]. The calculated crystallite size for  $\varepsilon$ -Fe<sub>3</sub>N nitride from (111) diffraction peak is found to be 29 nm and indicates the nanocrystalline nature of the materials.

The Co<sub>4</sub>N nitride crystallizes in fcc cubic structure having lattice parameters, a=3.55 Å, which is comparable with the literature reported values i.e. a=3.55 Å [11]. It is to be noted that Co<sub>4</sub>N and Co phases have almost the same XRD pattern. The value of lattice parameters (3.55 Å) of Co<sub>4</sub>N nitride is different from hexagonal Co metal, i.e. a=2.50 Å and c=4.06 Å. This discrepancy may be attributed to the presence of significant arrangement of nitrogen in the cubic lattice of Co<sub>4</sub>N, resulting to the lattice expansion. The crystallite size calculated for Co<sub>4</sub>N phase from (111) diffraction peak is 22 nm and indicates ultrafine nature of the materials. Based on the argument mentioned above, the XRD patterns have been indexed for  $\epsilon$ -Fe<sub>3</sub>N and Co<sub>4</sub>N phases and have been summarized in table no 2.

#### **3.3 SEM Studies**

Typical SEM photographs of  $\varepsilon$ -Fe<sub>3</sub>N and Co<sub>4</sub>N phases have been presented in fig 4. The particles appear as clusters, having sub-micron size of dimensions nearly 140 nm for  $\varepsilon$ -Fe<sub>3</sub>N phase (fig 4(a)). The fig 4(b) shows the spherical particle (size 120 nm) with narrow size dispersion for Co<sub>4</sub>N phase. The SEM particle sizes are larger compared to the crystallite sizes (i.e. 29 nm for  $\varepsilon$ -Fe<sub>3</sub>N phase and 22 nm for Co<sub>4</sub>N phase) and may be attributed to the larger cluster size due to larger surface area of the smaller crystallites.

#### 3.4 Magnetic Studies

The field dependence of magnetizations for  $\varepsilon$ -Fe<sub>3</sub>N and Co<sub>4</sub>N phases at room temperature are shown in fig 5. And the inset shows coercivities for the clarity reason. The plot of specific magnetization as a function of field inverse for  $\varepsilon$ -Fe<sub>3</sub>N and Co<sub>4</sub>N has been shown in fig 6. The  $\varepsilon$ -Fe<sub>3</sub>N and Co<sub>4</sub>N nitride phases having particle dimension 29 nm and 22 nm do not get saturated upto the field of 20 kOe indicating superparamagnetic nature of the materials. The specific magnetization measured in higher field strength (10-20 kOe) is found to be linear with 1/H and from the intercept on the magnetization axis, one can estimate the saturation magnetization. The values of saturation magnetizations for  $\varepsilon$ -Fe<sub>3</sub>N and Co<sub>4</sub>N phases are found to be 28.1 emu/g and 123.6 emu/g respectively. The coercive field of  $\varepsilon$ -Fe<sub>3</sub>N and Co<sub>4</sub>N phases are estimated to be 47 Oe and 74 Oe, respectively and indicates the soft magnetic nature of the materials.

In  $\varepsilon$ -Fe<sub>3</sub>N system, the magnetization is due to unbalanced charge distribution between spin up and down states [7, 26]. The 3d density of states (DOS) of Fe-atom can mixed with 2p DOS of N-atom which results in the electron exchange process and some sort of covalent bonding between Fe and N [7]. However, some kind of ionic bonding in the material cannot be excluded. The number of d-electrons in Fe is reduced and results in

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lowering of magnetization value compared to the  $\alpha$ -Fe, i.e. 222 emu/g [27]. Thus bulk saturation magnetization value for  $\epsilon$ -Fe<sub>3</sub>N nitride phase is found to be 123 emu/g [28]. The magnetic moment of  $\epsilon$ -Fe<sub>3</sub>N phase is affected by lattice expansion, nitrogen content and ultrafine nature of the material. In the present study, nitrogen content found to be larger, i.e.  $\epsilon$ -Fe<sub>3</sub>N<sub>1,33</sub>, compared to stoichiometric  $\epsilon$ -Fe<sub>3</sub>N phase. This may leads to lower intraband polarization in the nitride and the reduced magnetic moment. Also, decrease in the saturation magnetization value has been reported in ultrafine particle system compared to the bulk value [29, 30]. The decrease of magnetization has been attributed to the size effect and spin-canting at the surface of the nanocrystallite composing a particle. The observed saturation magnetization value for  $\epsilon$ -Fe<sub>3</sub>N phase, i.e. 28.1 emu/g, may be due to the above proposed magnetic order. It should be noted that, superparamagnetic assembly consists of highly magnetic  $\epsilon$ -Fe<sub>3</sub>N particles and the thermal randomization process reduces the magnetization value.

The saturation magnetization value for  $Co_4N$  material, i.e. 123.6 emu/g, is significantly smaller than the bulk cobalt metal, i.e. 162.5 emu/g [31]. In the  $Co_4N$  nitride material bonding between cobalt 3d level and nitrogen 2p level occurs, resulting in the decrease of unpaired electrons in cobalt 3d level due to spin paring effect. With decrease of particle size, sufficient surface fractions are present in the materials which are magnetically dead. For superparamagnetic system with a decrease in size, thermal effect becomes dominant. Such kinds of results have been reported in the literature [7, 32].

The value of coercivities in the fine particle system initially increases with decrease of particle dimensions, then remains constant and then again decreases. This is due to the fact that single domain state can have maximum coercivity as a result of magnetization reversal by spin rotation. With further decrease of particle dimension the coercivity value

decrease below the critical dimension. In this study, one could get coercivity of 47 Oe and 74 Oe for  $\varepsilon$ -Fe<sub>3</sub>N and Co<sub>4</sub>N phases, respectively. The values of coercivities are significantly lower and comparable with the literature reported values for  $\varepsilon$ -Fe<sub>3</sub>N and Co<sub>4</sub>N material [11, 24]. Therefore, the synthetic strategy for production of  $\varepsilon$ -Fe<sub>3</sub>N and Co<sub>4</sub>N material can be versatile for the production of highly magnetic nanoparticles for the soft magnetic applications.

#### 4. Conclusion

Nanocrystalline  $\varepsilon$ -Fe<sub>3</sub>N and Co<sub>4</sub>N nitride phases are synthesized first time by a newer precursor route. The precursor materials, i.e. tris(1,2-diaminoethane)iron(II) Chloride and tris(1,2-diaminoethane)cobalt(III) Chloride were mixed with urea in different molar ratios and heat treated under nitrogen atmosphere at various temperatures. Pure  $\varepsilon$ -Fe<sub>3</sub>N and Co<sub>4</sub>N nitride phases have been obtained by using precursor and urea in the molar ratios of 1:12. The nitridation of the precursors were carried out at various temperatures ranging from 450 to 900 <sup>0</sup>C for various time durations. The synthesized precursors were confirmed by FT-IR studies and characterized the nitride materials by using various techniques, such as XRD, SEM and magnetic measurements. The  $\varepsilon$ -Fe<sub>3</sub>N and Co<sub>4</sub>N phases crystallize in hexagonal and fcc cubic structures with overall lattice expansions. There is a reduction of unpaired d-electron of Fe and Co in  $\varepsilon$ -Fe<sub>3</sub>N and Co<sub>4</sub>N phases due to contribution from nitrogen 2p states. The number of unpaired electrons in transition metals is reduced for intra-band polarization and these lead to reduction in magnetic moments in the nitride materials. Further the decrease of magnetization has been attributed to size effect, superparamagnetic behaviour and spin canting at the surface of the materials. The values

of saturation magnetization for  $\varepsilon$ -Fe<sub>3</sub>N and Co<sub>4</sub>N phases are found to be significantly lower than those of the bulk materials, i.e. 28.1 emu/g and 123.6 emu/g, respectively. The coercivity values i.e. 47 Oe for  $\varepsilon$ -Fe<sub>3</sub>N and 74 Oe for Co<sub>4</sub>N phases are smaller than the bulk materials and these indicate the soft magnetic nature of the materials. This study demonstrates the synthesis of  $\varepsilon$ -Fe<sub>3</sub>N and Co<sub>4</sub>N nitrides in nano-crystalline form and studied for their interesting magnetic properties.

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**Table No 1.** The frequencies (cm<sup>-1</sup>) and assignments for the tris(1,2-diaminoethane)iron(II) Chloride and tris(1,2-diaminoethane)cobalt(III) Chloride.

[Fe(en) <sub>3</sub> ]Cl <sub>2</sub>	Bennett <i>et al.</i> *	[Co(en) <sub>3</sub> ]Cl <sub>3</sub>	Bennett <i>et al.</i> **	
Synthesised	(Wavenumber	Synthesised	(Wavenumber	Assignments
(Wavenumber cm <sup>-1</sup> )	cm <sup>-1</sup> )	(Wavenumber cm <sup>-1</sup> )	<b>cm</b> <sup>-1</sup> )	

3	3351 b	3320-3240	3510-3440 b	3296-3160	N-H stretch
3	3006 b	3145-2876	3205-3090 b	2922-2880	C-H stretch
1	1573 b	1602-1588	1567 b	1592	NH <sub>2</sub> Scissor
1	1498 b	1455	1465 s	1461-1450	CH <sub>2</sub> Scissor
1	388 w	1388-1365	1366 s	1390-1273 N	$H_2 + CH_2$ Wag
1	1322 s	1329	1322 m	1336	CH <sub>2</sub> twist
	-	-	-	1390	CH <sub>2</sub> Wag
	-	1296-1272	-	1273	NH <sub>2</sub> Wag
1	148 m	1148-1092	1162 s, 1122 m	1115	NH <sub>2</sub> twist
1	1033 s	1069-1018	1058 s	1036-1015	C-N stretch
	-	978-870		973	C-C stretch
	-	860	779 s	871	CH <sub>2</sub> rock
(	620 m	701-633	-	688	NH <sub>2</sub> rock
	-	508-486	584 w-462 w	525-444	Ring def.

Abbreviations: b-broad, s-strong, m-medium, w-weak. (\*)-Ref.20, (\*\*)-Ref.21.

Table No 2. X-Ray diffraction patterns of  $\epsilon$ -Fe<sub>3</sub>N and Co<sub>4</sub>N nitride phases

Phases	Miller indices	Inter planar	Inter planar	Indensity
Formed	hkl (obs.)	spacing (obs.) in Å	spacing (Cal.) in Å	(obs.)
002	2.200	2.205	20	
111	2.098	2.094	100	
112	1.614	1.619	20	
300	1.377	1.374	12	
113	1.250	1.250	12	
302	1.168	1.167	8	
Co <sub>4</sub> N	111	2.053	2.049	100
	200	1.778	1.775	30
	220	1.256	1.255	22
	C,			

#### **CAPTIONS FOR FIGURES**

Fig 1. The FT-IR transmittance spectrum of tris(1,2-diaminoethane)iron(II) Chloride.

Fig 2. The FT-IR transmittance spectrum of tris(1,2-diaminoethane)cobalt(III) Chloride.

Fig 3. XRD patterns of various nitrides synthesized by using metal precursor: urea ratios of 1:12, (a)  $\varepsilon$ -Fe<sub>3</sub>N phase at 550 <sup>o</sup>C and (b) Co<sub>4</sub>N phase at 800 <sup>o</sup>C.

Fig 4. SEM Photographs for (a)  $\varepsilon$ -Fe<sub>3</sub>N phase and (b) Co<sub>4</sub>N phase.

**Fig 5.** Plot of Specific magnetization as a function of field for (a)  $\varepsilon$ -Fe<sub>3</sub>N phase and (b) Co<sub>4</sub>N phase. Inset shows coercivity for (a)  $\varepsilon$ -Fe<sub>3</sub>N phase and (b) Co<sub>4</sub>N phase.

Fig 6. Plot of specific magnetization as a function of  $H^{-1}$  for (a)  $\epsilon$ -Fe<sub>3</sub>N and (b) Co<sub>4</sub>N phases.

#### GRAPHICAL ABSTRACT

Nanocrystalline  $\varepsilon$ -Fe<sub>3</sub>N and Co<sub>4</sub>N nitride phases are synthesized first time by newer chemical routes. The  $\varepsilon$ -Fe<sub>3</sub>N phase crystallizes in hexagonal structure with unit cell parameters, a=4.76 Å and c=4.41 Å. The Co<sub>4</sub>N phase crystallizes in face centered cubic (fcc) structure with unit cell parameters, a=3.55 Å. The estimated crystallite size for  $\varepsilon$ -Fe<sub>3</sub>N and Co<sub>4</sub>N phases are 29 nm and 22 nm, respectively. The values of saturation magnetization for  $\varepsilon$ -Fe<sub>3</sub>N and Co<sub>4</sub>N phases are found to be 28.1 emu/g and 123.6 emu/g respectively. The reduction of magnetic moments in ultrafine materials compared to bulk materials have been explained by fine particle size and surface effects. We have synthesized the high moment  $\varepsilon$ -Fe<sub>3</sub>N and Co<sub>4</sub>N nitride with reduced coercivity which may find applications as soft magnetic materials.



#### Highlight

- Nanocrystalline  $\varepsilon$ -Fe<sub>3</sub>N and Co<sub>4</sub>N nitride phases are synthesized.
- The  $\epsilon$ -Fe<sub>3</sub>N and Co<sub>4</sub>N crystallizes in hexagonal and fcc structure respectively.
- The observed magnetic parameters indicates soft magnetic properties.
- The magnetic properties have been explained on the basis of fine particle magnetism.



FIGURE 1



FIGURE 2



FIGURE 3

# ACCEPTED MANUSCRIPT



# FIGURE 4





FIGURE 5





FIGURE 6