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(54) Title: A PROCESS FOR THE SYNTHESIS OF NANOPARTICLES OF TRANSITION METAL CHALCOGENIDES

A_x-B_y
Formula (I)

(57) Abstract: The present invention relates to a process for the synthesis of transition metal chalcogenides (TMC) having formula (I). More particularly, the present work relates to a one pot single phase process for the synthesis of TMC system having formula (I) by wet chemistry.

WO 2020/222249 A1

A PROCESS FOR THE SYNTHESIS OF NANOPARTICLES OF TRANSITION METAL CHALCOGENIDES

FIELD OF THE INVENTION:

The present invention relates to a process for the synthesis of transition metal chalcogenides (TMC) having formula (I). More particularly, the present work relates to a one-pot single phase process for the synthesis of TMC system having formula (I) by wet chemistry.

BACKGROUND AND PRIOR ART OF THE INVENTION:

Transition-metal chalcogenides represent an important class of materials with rich phase diagram and industrial applications. The electronic (optical, magnetic, and electrical) and thermal properties are so sensitive to the crystalline phase, stoichiometry, shape, size that it is essential to reach a good control over the chemistry of phase formation. TMC consisting of metal atoms (Fe, Co, and Ni) and chalcogen atoms (S, Se, Te) have renewed interest as very attractive candidates for applications in devices including fuel-cells, solar-cells, light-emitting-diodes, sensors, memory-devices, thermoelectric devices, supercapacitors, Li- ion batteries, magnetic materials etc. Among the TMC, Fe_xSe_y compounds (with x: y varying from 1:2 to 1:1) are of great importance because of their interesting and unique magnetic, electrical, thermal, and optical properties which are strongly related on the stoichiometric ratio between Fe and Se as well as their crystalline structure. Family of iron selenides have four stable phases: $FeSe_2$, Fe_3Se_4, Fe_7Se_8, and FeSe having orthorhombic (O) marcasite, monoclinic (M) and hexagonal (H) NiAs type, and tetragonal (T) PbO type crystal structure, respectively. Existence of multiple phases with abundantly different crystal structures indicates the complexity of the system and therefore, phase-selective syntheses were quite challenging for this system. In solid state method, as reported by Grivel *et al.* (Supercond. Sci. Technol. 24 (2011) 015007) there was phase transformation of Fe-Se system with respect to temperature in a sequence of $FeSe_2 \rightarrow Fe_3Se_4 \rightarrow Fe_7Se_8 \rightarrow$ β-FeSe at 300 °C, 320 °C, ~ 340 °C, 350 °C - 370 °C, respectively. In this article the phase boundaries were not sharply defined as a function of temperature. Often at a particular temperature, phases evolved out of the other phases leading to overall impurity.

Numerous solution processes have been applied to synthesize these compounds. For example, Fe_3Se_4 and Fe_7Se_8 nanoparticles (NPs) were obtained via the thermal decomposition method at 340 °C-350 °C, Fe_3Se_4 were synthesized at 300 °C by one-pot high-temperature organic-solution-phase method, flower-like $FeSe_2$ NPs were synthesized

via a solvothermal approach at 200 °C, $FeSe_x$ (x=1,2) NPs were synthesized via the hot-injection method at 330 °C and $FeSe_2$ NPs were synthesized via hydrothermal method at 140 °C for 13 h. The FeSe NPs were synthesized by solvothermal reaction in an autoclave at 220 °C for 24 h. These methods involved the high temperature, long reaction time, complex apparatus, expensive chemicals, or drastic conditions to synthesis the Fe-Se NPs.

Thus, adopting a simple, low-temperature, short-time, and low-cost method with well-defined shape and high crystallinity of Fe-Se NPs is much desired. To overcome the prior drawbacks the present invention provides a one pot single phase process for the synthesis of transition metal chalcogenides (TMC) system having formula I.

OBJECTIVES OF THE INVENTION:

The objective of the present invention is to provide a one pot single phase process for the synthesis of transition metal chalcogenides (TMC) having formula (I).

SUMMARY OF THE INVENTION:

Accordingly, the present invention provides a one pot single phase process for the synthesis of transition metal chalcogenides (TMC) system having formula (I) by using wet chemistry. This method comprises mixing both precursors of transition metal and chalcogen in the presence of a reducing agent and an accelerating agent at a temperature in the range of 100 °C to 300 °C for a time period varied from 30 min to 10 h to obtain transition metal chalcogenides (TMC) having formula (I).

The transition metal chalcogenides (TMC) system having formula (I) is represented as

$$A_x\text{-}B_y$$

Formula (I)

wherein,

A is selected from iron, chromium, manganese, cobalt, or nickel.

B is selected from selenium, sulphur, or tellurium.

The A_x-B_y is selected from AB_2, A_3B_4, A_7B_8 or AB,

wherein x and y are in ranges from 1:2 to 1:1.

BRIEF DESCRIPTION OF THE DRAWINGS

Figure 1: Powder X-ray diffraction patterns collected at various temperatures during the heating ramp a. 25 °C b. 190 °C c. 360 °C d. 394 °C and e. 486 °C for prior art.

Figure 2: Powder X-ray diffraction patterns collected at various temperatures during the heating ramp for present invention.

Figure 3: Iron - Selenium phase diagram.

Figure 4: XRD patterns of the as-synthesized a) $FeSe_2$ NPs, b) Fe_3Se_4 NPs, c) Fe_7Se_8 NPs and d) FeSe NPs.

Figure 5: Magnetization (M) vs. applied magnetic field (H) hysteresis loops of a) $FeSe_2$ b) Fe_3Se_4 c) Fe_7Se_8 and d) FeSe measured by the vibrating sample magnetometer at 300 K.

Figure 6: Magnetization (M) vs. applied magnetic field (H) hysteresis loops of a) $FeSe_2$ b) Fe_3Se_4 c) Fe_7Se_8 and d) FeSe measured by the vibrating sample magnetometer at 10 K.

Figure 7: TEM measurements of as-synthesized NPs.

Figure 8: Thermal Gravimetric Analysis (TGA).

Figure 9: Raman spectra.

Figure 10: TEM images of as-synthesized NPs with different organic solvents.

Figure 11: XRD patterns of the as-synthesized Co_3Se_4 NPs.

Figure 12: XRD patterns of the as-synthesized Ni_3Se_4 NPs.

Figure 13: XRD patterns of the as-synthesized MnSe NPs.

Figure 14: XRD patterns of the as-synthesized Fe_3Se_4 NPs with different crystallite size.

Figure 15: Magnetization (M) vs. applied magnetic field (H) hysteresis loops of Fe_3Se_4 NPs with different crystallite size measured by the vibrating sample magnetometer at 300 K.

Figure 16: Coercive field (H_c) and remanence magnetization (M_r) vs. crystallite size of Fe_3Se_4 NPs.

DETAILED DESCRIPTION OF THE INVENTION

The invention will now be described in detail in connection with certain preferred and optional embodiments, so that various aspects thereof may be more fully understood and appreciated.

The present invention provides a one-pot single phase process for the synthesis of a transition metal chalcogenide (TMC) nanoparticles (NPs) system having formula (I) by using wet chemical method, the process comprising mixing and stirring both a transition metal precursor and a chalcogen precursor in the presence of a reducing agent and an accelerating agent and stirring at a temperature in the range of 100 °C to 300 °C for a time period varied from 30 min to 10 h to obtain the TMC NPs system having formula (I).

The TMC NPs system having formula (I) is represented as

$$A_x\text{-}B_y$$

Formula (I)

wherein,

A is selected from the group consisting of iron, chromium, manganese, cobalt, and nickel;

B is selected from the group consisting of selenium, sulphur, and tellurium;

A_x-B_y is selected from AB_2, A_3B_4, A_7B_8 and AB;

wherein the ratio of x and y are in ranges from 1:2 to 1:1.

The system of formula (I) is selected from $FeSe_2$, Fe_3Se_4, Fe_7Se_8, FeSe, Co_3Se_4, Ni_3Se_4 and MnSe.

The size of as-synthesized TMC NPs are in the range of 5 nm to 350 nm. The shape of as-synthesized TMC NPs is selected from nano-rod, nano-sphere, nano-sheet, nano-platelet, nano-cube, and mixed shape.

Any organic solvent, which has the ability to make complex with transition metal (Fe) and chalcogen (Se) precursors, and simultaneously reduce them can be used as a reducing agent for TMC system. Moreover, any organic solvent can use as an accelerating agent which have the ability to make complex with chalcogen (Se powder). The particular temperature required for pure phase formation will strongly depends on the organic solvent. As going towards the stronger reducing and accelerating agent, the temperature and time for that particular phase changes.

The reducing agent is selected from oleylamine (OLA), oleic acid, 1-octadecene (1-ODE), octadecylamine, oleyl alcohol, pentylamine, ethylamine and n-octadecane.

The accelerating agent is selected from 1-octadecene, oleic acid, oleylamine, octadecylamine, oleyl alcohol, pentylamine, and ethylamine.

The transition metal precursor is selected from Tris(acetylacetonato) iron (III) ($Fe(acac)_3$), Cobalt(III) acetylacetonate, Nickel(II) acetylacetonate and Manganese(III)acetylacetonate.

The chalcogen precursor is Se powder.

In one of the features, the present invention provides a one pot single phase process for the synthesis of transition metal chalcogenides (TMC) nanoparticles system particularly Fe-Se system comprising the steps of:

a) mixing Se powder and $Fe(acac)_3$ at room temperature (25 °C to 30 °C) in the presence of an organic solvent under the blanket of inert gas with constant magnetic stirring;

b) raising the temperature to 40 °C followed by stirring for 30 min and taking the first sample of only Se powder;

c) further increasing the temperature to 50 °C followed by stirring for 30 min and taking the second sample of only Se powder and

d) increasing the temperature up to 340 °C with the rate of 10 °C/30 min and taking the sample at every 10 °C rise in temperature, as the temperature increases, $FeSe_2$ starts forming followed by Fe_3Se_4, Fe_7Se_8 and FeSe.

In each step 2 mL aliquots are withdrawn using a long needle-glass syringe. All the samples are stored in small glass vials and naturally quenched to room temperature (RT) for further investigation.

In another feature of the present invention, the organic solvent is selected from oleylamine (OLA); oleylamine & 1-octadecene (OLA & 1-ODE) and oleylamine (OLA) & pre-dissolved Se powder in 1-octadecene (1-ODE).

Three separate reactions are carried out with above procedure except the solvent conditions; in one reaction only OLA has been used as a solvent, in second reaction a combination of OLA and 1-ODE (in 3:2 ratio) has been used as a solvent; and in the last reaction Se powder was pre-dissolved in 1-ODE and used that as a Se precursor with OLA and $Fe(acac)_3$.

Figure 1 depicts diffraction patterns collected at various temperatures during the heating ramp for prior art. The phase boundaries were not sharply defined as a function of temperature. Often at a particular temperature, phases evolved out of the other phases leading to overall impurity.

Figure 2 depicts diffraction patterns collected at various temperatures during the heating ramp for present invention. Phase boundaries were mostly sharply defined and well isolated as a function of temperatures and phase impurities were avoided. The diffraction pattern shows the phase evolution from $FeSe_2$ to Fe_3Se_4 followed by Fe_7Se_8 and FeSe.

Table 1. Results of diffraction patterns collected at various temperatures during the heating ramp.

Reaction	Fe Precursor	Se precursor	Solvent	Temperature-range	Phase
A	$Fe(acac)_3$	Se powder	OLA	RT – 100 °C	Se
				110 – 130 °C	Se + $FeSe_2$
				140 – 220 °C	$FeSe_2$
				230 – 240 °C	$FeSe_2$ + Fe_3Se_4
				250 – 270 °C	Fe_3Se_4
				280 – 340 °C	Fe_7Se_8
B	$Fe(acac)_3$	Se powder (Se was pre –	OLA + 1-ODE	RT – 100 °C	Se
				110 – 230 °C	$FeSe_2$

		dissolved in 1-ODE at 30 °C for 6 h)		240 – 250 °C	$FeSe_2$ + Fe_3Se_4
				260 °C	Fe_3Se_4 + $FeSe_2$
				270 °C	Fe_7Se_8
				280 – 300 °C	FeSe

Figure 3 depicts Iron - Selenium phase diagram. Phases 1 to 5 show the results of five prolonged reactions. The experiments were done by varying the amount of Se from 37.5 to 100 at % with constant Fe precursor in presence of OLA and 1-ODE together from RT to 340 °C. The phase transformation has been confirmed by doing the WAXS (wide angle X-ray scattering) of all the samples, taken at every 10 °C rise in temperature from 30 °C - 340 °C and the data are compared with the JCPDS files to conform the phases.

Table 2: Results of phases formed at minimal possible temperature with pertinent time.

Phases	**Solvent**	**Ramping Rate**	**Temp.**	**Time**	**Remarks**
$FeSe_2$	OLA	2 °C min^{-1}	150 °C	2 h	Single phase $FeSe_2$ NPs
Fe_3Se_4	OLA	2 °C min^{-1}	230 °C	8 h	Fe_3Se_4 + $FeSe_2$ (impurity phase)
		2 °C min^{-1}	240 °C	6 h	
		2 °C min^{-1}	250 °C	5 h	
		120 °C - 0.5 h + 2 °C min^{-1} up to 200 °C + 2 °C min^{-1} up to 250 °C	250 °C	4 h	Fe_3Se_4 + $FeSe_2$ (impurity phase)
		2 °C min^{-1}	260 °C	5 h	
		120 °C - 0.5 h + 2 °C min^{-1} up to 200 °C + 2 °C min^{-1} up to 250 °C	260 °C	2 h	Single phase Fe_3Se_4 NPs
Fe_7Se_8	OLA	2 °C min^{-1}	270 °C	4 h	Fe_3Se_4 + $FeSe_2$ (impurity phase)
		5 °C min^{-1} up to 230 °C + 2 °C min^{-1} up to 270 °C	270 °C	4 h	Fe_7Se_8 + Fe_3Se_4 (impurity phase)
		2 °C min^{-1}	280 °C	4 h, 5 h	
		5 °C min^{-1} up to 230 °C + 2 °C min^{-1} up to 280 °C	280 °C	4 h	Single phase Fe_7Se_8 NPs
	OLA	5 °C min^{-1} up to 230 °C + 2 °C min^{-1} up to 280 °C	280 °C	4 h	Fe_7Se_8

	OLA + 1-ODE	5 °C min^{-1} up to 230 °C + 2 °C min^{-1} up to 280 °C	280 °C	4 h	FeSe + Fe_7Se_8 (impurity phase)
	OLA + 1-ODE	5 °C min^{-1} up to 230 °C + 2 °C min^{-1} up to 280 °C	280 °C	4 h	Single phase FeSe NPs (Se powder was pre-dissolved in 1-ODE)

Figure 4 depicts XRD patterns of the as-synthesized a) $FeSe_2$ NPs, b) Fe_3Se_4 NPs, c) Fe_7Se_8 NPs, and d) FeSe NPs. All the XRD peaks are in good agreement with the JCPDS (Joint Committee on Powder Diffraction Standards) data files— (74-0247) for $FeSe_2$, (73−2021) for Fe_3Se_4, (71−0586) for Fe_7Se_8 and (85−0735) for FeSe without ambiguous reflections. The XRD and magnetic measurements prove the high purity of as-synthesized NPs. Crystallite size of $FeSe_2$ = 23 nm, Fe_3Se_4 = 35 nm, Fe_7Se_8 = 29 nm, FeSe = 46 nm as estimated from the XRD pattern using Scherrer's formula.

Figure 5 depicts magnetization (M) vs. magnetic field (H) hysteresis loops of a) $FeSe_2$ b) Fe_3Se_4 c) Fe_7Se_8 and d) FeSe measured by the vibrating sample magnetometer at 300 K in an applied magnetic field up to ±60 kOe. The M-H curves reveal prominent M-H characteristics indicating the synthesis of pure phase. Figure a) shows the M-H curve of $FeSe_2$ NPs revealing paramagnetic behavior with coercivity (H_c) 146 Oe. Figure b-c) shows the M-H curves of Fe_3Se_4 and Fe_7Se_8 NPs having ferrimagnetic behavior. These hysteresis loops show the coercivity 1.6 kOe and 1.8 kOe, respectively. In Figure d) the hysteresis loop of FeSe reveals ferromagnetic nature of NPs having coercivity (H_c) 282 Oe.

Figure 6 depicts M-H hysteresis loops of a) $FeSe_2$ b) Fe_3Se_4 c) Fe_7Se_8 and d) FeSe measured by the vibrating sample magnetometer at 10 K. The coercivity (H_c) of $FeSe_2$ NPs rises to 200 Oe with ferromagnetic behavior. The H_c value of Fe_3Se_4 nanorods raises nearly 20-fold to about 32 kOe. The H_c value of Fe_7Se_8 nanorods rises more than 7-fold to about 13.8 kOe. The coercivity (H_c) of FeSe nanorods increases to about 4.4 kOe.

Table 3: Magnetic parameters measured at 300 K and 10 K for Fe-Se system. H_c and σ_R represents the coercivity and remanence respectively obtained from hysteresis loops at various temperature.

Phases	H_c (Oe)		σ_R (emu/g)	
	300 K	10 K	300 K	10 K
$FeSe_2$	146	200	~ 0	0.4
Fe_3Se_4	1600	32000	1.2	7.3
Fe_7Se_8	1800	13800	2	8.6
FeSe	300	4400	0.1	0.4

Figure 7 shows TEM measurements of as-synthesized NPs. Typical TEM images of as-synthesized a)$FeSe_2$, b)Fe_3Se_4, c)Fe_7Se_8 and d)FeSe NPs shows the rod like features and inset shows the iron selenide nanocacti with rod like features growing on the surface [Scale bar in the insets are 100 nm]. a') to d') shows the lattice fringes space at 2.5 Å, 2.7 Å, 5.4 Å and 5.5 Å represents the (111), (-202), (101) and (001) of Fe-Se system respectively [The inset SAED pattern]. The diffraction pattern obtained for all the nanostructures were matched well with the crystal planes of Fe-Se system and have been assigned to (002), (101), (111) planes for $FeSe_2$, (-202), (011) planes for Fe_3Se_4, (203), (101), (206) planes for Fe_7Se_8 and (001), (101) planes for FeSe. Thus, d-spacing calculated in TEM are in good agreement with those given in the standard JCPDS for all the phases of Fe-Se system.

Figure 8 shows Thermal Gravimetric Analysis (TGA). All the samples were undergone with different step decomposition. The first step in all samples is related to the loss of all organic fragments capped on NPs, this step was up to 460 °C. The $FeSe_2$ NPs further go through three more step decomposition. The steps assigned to the decomposition of $FeSe_2$ NPs to Fe_3Se_4; Fe_3Se_4 NPs to the Fe_7Se_8 followed by the conversion of Fe_7Se_8 to FeSe and final step, the decomposition of FeSe NPs started at 875 °C and remains up to 1000 °C. The Fe_3Se_4 NPs further go through final step, assigned to the decomposition of Fe_3Se_4 started at 725 °C and gradually decreases up to 1000 °C. The Fe_7Se_8 NPs go through final step, assigned to the decomposition of Fe_7Se_8 started at 770 °C and gradually decreases up to 1000 °C. The FeSe NPs go through final step assigned to the decomposition of FeSe started at 875 °C and gradually decreases up to 1000 °C.

Figure 9 shows Raman Spectra of all the samples having six characteristic peaks at 225, 244, 292, 410, 496, and 611 cm^{-1}. The presences of Fe–Se near 225 cm^{-1}, 292 $cm^{-1}$and 610 cm^{-1}, as well as Fe–O at 410 cm^{-1} are identified for all the samples.

Figure 10 shows TEM images of as-synthesized NPs in the presence of different organic solvents a) n-octadecane, b) 1-octadecene, c) octadecylamine and d) oleylamine. TEM data shows the strong depends of size, shape, and stability on solvent. Figure shows the as-synthesized nanospheres in presence of n-octadecane, nanoplatelets in 1-octadecene, nano-spheres in octadecylamine and nanocacti with rod like features growing on the surface in OLA.

To control the size of transition metal chalcogenides (Fe_3Se_4), the reaction parameters are optimized to find suitable synthesis conditions to crystallize various sizes of Fe_3Se_4 compound by following the one-pot thermal decomposition method as shown in table 4 and the observed data shows that as the reaction temperature increases crystallite size also increases, table 5.

Table 4: Summary of the experimental conditions to control the size of the Fe_3Se_4 NPs.

Reaction	Solvent	Fe precursor	Se precursor	Step 1		Step 2		Results
				Temp. (°C)	Time (min)	Temp. (°C)	Time (min)	
1	OLA	$Fe(acac)_3$	Se powder	120	30	260	120	S1
2						300	80	S2
3						330	70	S3

Table 5 describes list of calculated crystallite size along different planes of all the as-synthesized Fe_3Se_4 NPs, indicating the influence of the temperature on the crystallite size of the products evolve out of solution chemistry.

Table 5: List of calculated crystallite size along different planes of all the as-synthesized Fe_3Se_4 NPs

Sample	Crystallite size along following planes: d (± 3 nm)		
	(-112)	(202)	(204)
S1	33	25	22
S2	37	31	24
S3	42	35	26

Figure 11 depicts XRD patterns of the as-synthesized Co_3Se_4 NPs. The XRD peaks are in good agreement with the 99989-ICSD (Inorganic Crystal Structure Database) data file without ambiguous reflections.

Figure 12 depicts XRD patterns of the as-synthesized Ni_3Se_4 NPs. The XRD peaks are in good agreement with the JCPDS (Joint Committee on Powder Diffraction Standards) data files— (65-1220) without ambiguous reflections.

Figure 13 depicts XRD patterns of the as-synthesized MnSe NPs. The XRD peaks are in good agreement with the JCPDS (Joint Committee on Powder Diffraction Standards) data files— (65-7705) without ambiguous reflections.

Figure 14 depicts XRD patterns of the as-synthesized Fe_3Se_4 NPs with different crystallite size. The XRD peaks are in good agreement with the JCPDS (Joint Committee on Powder Diffraction Standards) data files— (73-2021) without ambiguous reflections.

Figure 15 depicts M-H hysteresis loops of S1, S2 and S3 of Fe_3Se_4 measured by the vibrating sample magnetometer at 300 K in an applied magnetic field up to ±60 kOe.

Figure 16 depicts coercive field (H_c) vs crystallite size (left) and remanence magnetization (M_r) vs crystallite size (right) for Fe_3Se_4 NPs.

Examples: Following examples are given by way of illustration therefore should not be construed to limit the scope of the invention.

Example 1: Synthesis of the Fe–Se System to Examine the Phase Transformation

Synthesis of the Fe–Se System in OLA and 1-ODE. To study the effect of stoichiometry on the phase-transformation five prolonged reactions were performed by varying the amount of Se from 37.5 to 100 wt %, the stoichiometry of Fe/Se ranging from 1:0.75 (0.35 g, 0.059 g) to 1:2 (0.35 g, 0.158 g). All the reactions were carried out in the presence of 10 mL of 1-ODE and 15 mL of OLA in a 100 mL three-neck round-bottom (RB) flask under the blanket of nitrogen with constant magnetic stirring. The temperature was raised from 30 to 340 °C at a ramping rate of 2 °C min^{-1}. For every 10 °C rise in the temperature, hold-time was ~30 min. In each step, 2 mL aliquots were withdrawn using a long needle glass syringe to study the phase evolution. All the samples were stored in small glass vials and naturally quenched to RT for further investigation by wide-angle X-ray scattering (WAXS). The phase diagram was plotted after assembling the WAXS results, which inferred the effect of stoichiometry along with temperature on phase transformation of the Fe–Se system.

Example 2: Synthesis of the Fe–Se System in OLA

To study the effect of solvents on phase transformation one synthesis was done by following the same procedure as mentioned above except that only the OLA (15 mL) was used as an organic solvent with the stoichiometry of 1:1.

Example 3: Synthesis of the Fe–Se System in OLA and Predissolved Se Powder in 1-ODE

In order to examine the effect of solvents, one more reaction was done with the same procedure as mentioned earlier except that the Se powder was predissolved in 1-ODE under a nitrogen environment with constant magnetic stirring at 30 °C for 6 h.

Example 4: Synthesis of $FeSe_2$ NPs

In a conventional reaction, 0.353 g (1 mmol) of $Fe(acac)_3$ and 0.158 g (2 mmol) of Se powders were added to 15 ml of OLA in a 100 mL three-neck round bottom (RB) flask. The mixture was stirred under a flow of high-purity nitrogen gas at 30 °C. Then the temperature was raised to 150 °C at a ramping rate of 2 °C min^{-1} and kept at 150 °C for 2 h. A thermometer was placed inside the RB-flask and the temperature was kept stable within ±1.0 °C during the 2 h long dwell-time at 150 °C. The solution was cooled to RT by removing the heating source. After cooling, 20 ml of 2-propanol was added to the solution to give a black precipitate, which was separated from the solution by centrifugation. The obtained NPs were rewashed with the mixture of 15 ml hexane and 10 ml 2-propanol. Finally, the product was dried in a vacuum at 28°C and utilized for further characterization.

Example 5: Synthesis of Fe_3Se_4 NPs

A 0.53 g (1.5 mmol) portion of $Fe(acac)_3$ and 0.158 g (2 mmol) of Se powder were mixed in 15 mL of OLA in a 100 mL three-neck RB flask. The mixture was heated to 120 °C and maintained for 30 min. Then, the temperature was raised at a heating rate of 2 °C min^{-1} up to 200 °C and 5 °C min^{-1} was used to reach a maximum temperature of 260 °C; at which the sample was maintained for 2 h.

Example 6: Synthesis of Fe_7Se_8 NPs

A 0.618 g (1.75 mmol) of $Fe(acac)_3$ and 0.158 g (2 mmol) of Se powder were added in 15 mL of OLA in a 100 mL three-neck RB flask. The mixture was heated to the designed temperature at a ramping rate of 5 °C min^{-1} from 30 °C to 230 °C and then after ramping rate was decreased to 2 °C min^{-1} up to 280 °C, and kept for 4 h.

Example 7: Synthesis of FeSe NPs

This synthesis is similar to the synthesis of Fe_7Se_8 NPs with stoichiometry 1:1 except that the Se powder was pre-dissolved in 11 mL of 1-ODE at 30 °C with constant magnetic stirring for 6 h.

Example 8: Synthesis with different solvents

These syntheses are similar to the above synthesis except that 1-octadecene, octadecylamine and n-octadecane was used instead of OLA.

Example 9: Synthesis of Co_3Se_4 NPs

A 1.5 mmol portion of Cobalt(III) acetylacetonate ($Co(acac)_3$) and 2 mmol of Se powder were mixed in 15 mL of OLA in a 100 mL three-neck RB flask. The mixture was heated to 120 °C and maintained for 30 min. Then, the temperature was raised at a heating rate of 2 °C min^{-1} up to 200 °C and 5 °C min^{-1} was used to reach a maximum temperature of 300 °C; at which the sample was maintained for 2 h.

Example 10: Synthesis of Ni_3Se_4 NPs

A 1.5 mmol portion of Nickel(II) acetylacetonate ($Ni(acac)_2$) and 2 mmol of Se powder were mixed in 15 mL of OLA in a 100 mL three-neck RB flask. The mixture was heated to 120 °C and maintained for 30 min. Then, the temperature was raised at a heating rate of 2 °C min^{-1} up to 200 °C and 5 °C min^{-1} was used to reach a maximum temperature of 300 °C; at which the sample was maintained for 2 h.

Example 11: Synthesis of MnSe NPs

A 2 mmol portion of Manganese(III)acetylacetonate ($Mn(acac)_3$) and 2 mmol of Se powder were mixed in 15 mL of OLA in a 100 mL three-neck RB flask. The mixture was heated to 120 °C and maintained for 30 min. Then, the temperature was raised at a heating rate of 2 °C min^{-1} up to 200 °C and 5 °C min^{-1} was used to reach a maximum temperature of 300 °C; at which the sample was maintained for 2 h.

Advantages of the invention:

1. The present method is simpler and economical than solid state route and required relatively lower temperature.
2. This method is capable of giving high purity in phases and by this route it is easy to control the size, shape, and crystalline structure.
3. It is possible to control the size of NPs by varying the temperature with pertinent time as well as shape by changing the solvents.
4. This route is not only applicable for these 4 phases but also for other iron chalcogenide phases.

5. Various other transition metal chalcogenides consisting of metal atoms (Fe, Cr, Mn, Co, and Ni) and chalcogen atoms (S, Se, Te) can also be synthesized by this route after optimizing the reaction conditions (temperature, precursors, solvents).

Claims:

1. A one pot single phase process for the synthesis of a transition metal chalcogenide nanoparticle system having formula (I) by using wet chemical method, the process comprising mixing and stirring both a transition metal precursor and a chalcogen precursor in the presence of a reducing agent and an accelerating agent and stirring at a temperature in the range of 100 °C to 300 °C for a time period varied from 30 min to 10 h to obtain the transition metal chalcogenide nanoparticle system having formula (I),

   wherein

   the formula (I) is represented as

   Ax-By

   Formula (I)

   wherein,

   A is selected from the group consisting of iron, chromium, manganese, cobalt, and nickel;

   B is selected from the group consisting of selenium, sulphur, and tellurium;

   Ax-By is selected from AB_2, A_3B_4, A_7B_8 and AB;

   wherein the ratio of x and y are in ranges from 1:2 to 1:1.

2. The process as claimed in claim 1, wherein said system of formula (I) is selected from $FeSe_2$, Fe_3Se_4, Fe_7Se_8, FeSe, Co_3Se_4, Ni_3Se_4 and MnSe.
3. The process as claimed in claim 1, wherein the size of as-synthesized transition metal chalcogenide nanoparticle is in the range of 5 nm to 350 nm.
4. The process as claimed in claim 1, wherein the shape of as-synthesized transition metal chalcogenide nanoparticle is selected from nano-rod, nano-sphere, nano-sheet, nano-platelet, nano-cube and mixed shape.
5. The process as claimed in claim 1, wherein the reducing agent is selected from oleylamine, oleic acid, 1-octadecene, octadecylamine, oleyl alcohol, pentylamine, ethylamine and n-octadecane.
6. The process as claimed in claim 1, wherein the accelerating agent is selected from 1-octadecene, oleic acid, oleylamine, octadecylamine, oleyl alcohol, pentylamine, and ethylamine.
7. The process as claimed in claim 1, wherein the transition metal precursor is selected from Tris(acetylacetonato) iron (III), Cobalt(III) acetylacetonate, Nickel(II) acetylacetonate and Manganese(III)acetylacetonate.
8. The process as claimed in claim 1, wherein the chalcogen precursor is Se powder.

9. A one pot single phase process for the synthesis of transition metal chalcogenides nanoparticles system wherein said system is Fe-Se system comprising the steps of:
   a) mixing Se powder and $Fe(acac)_3$ at a temperature in the range of 25 °C to 30 °C in the presence of an organic solvent under the blanket of inert gas with constant magnetic stirring;
   b) raising the temperature to 40 °C followed by stirring for 30 min and taking the first sample of only Se powder;
   c) further increasing the temperature to 50 °C followed by stirring for 30 min and taking the second sample of only Se powder; and
   d) increasing the temperature up to 340 °C with the rate of 10 °C/30 min and taking the sample at every 10 °C rise in temperature, as the temperature increases, $FeSe_2$ starts forming followed by Fe_3Se_4, Fe_7Se_8 and FeSe.
10. The process as claimed in claim 9, wherein said organic solvent is selected from oleylamine; oleylamine & 1-octadecene; and oleylamine & pre-dissolved Se powder in 1-octadecene.

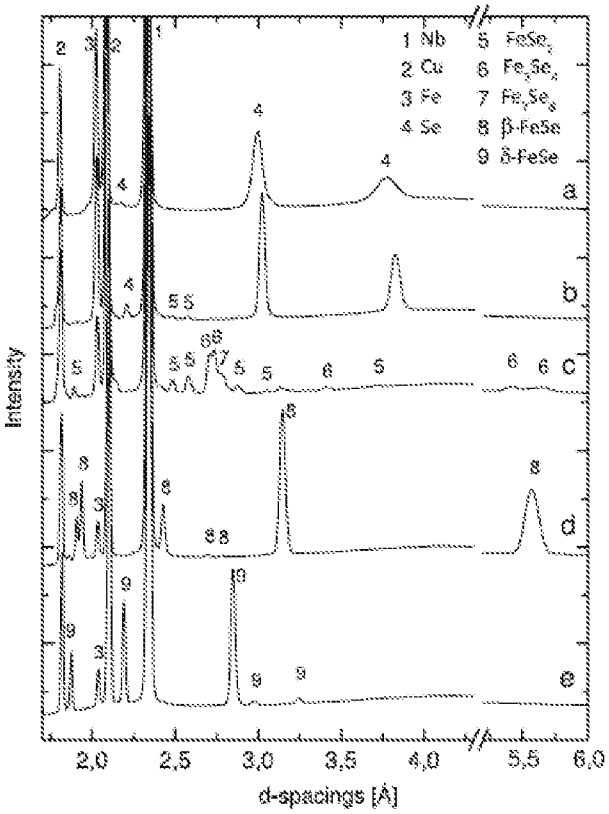
1 Nb
2 Cu
3 Fe
4 Se
5 FeSe2
6 Fe3Se4
7 Fe7Se8
8 β-FeSe
9 δ-FeSe
a
b
c
d
e
Intensity
2,0
2,5
3,0
3,5
4,0
5,5
6,0
d-spacings [Å]

Figure 1

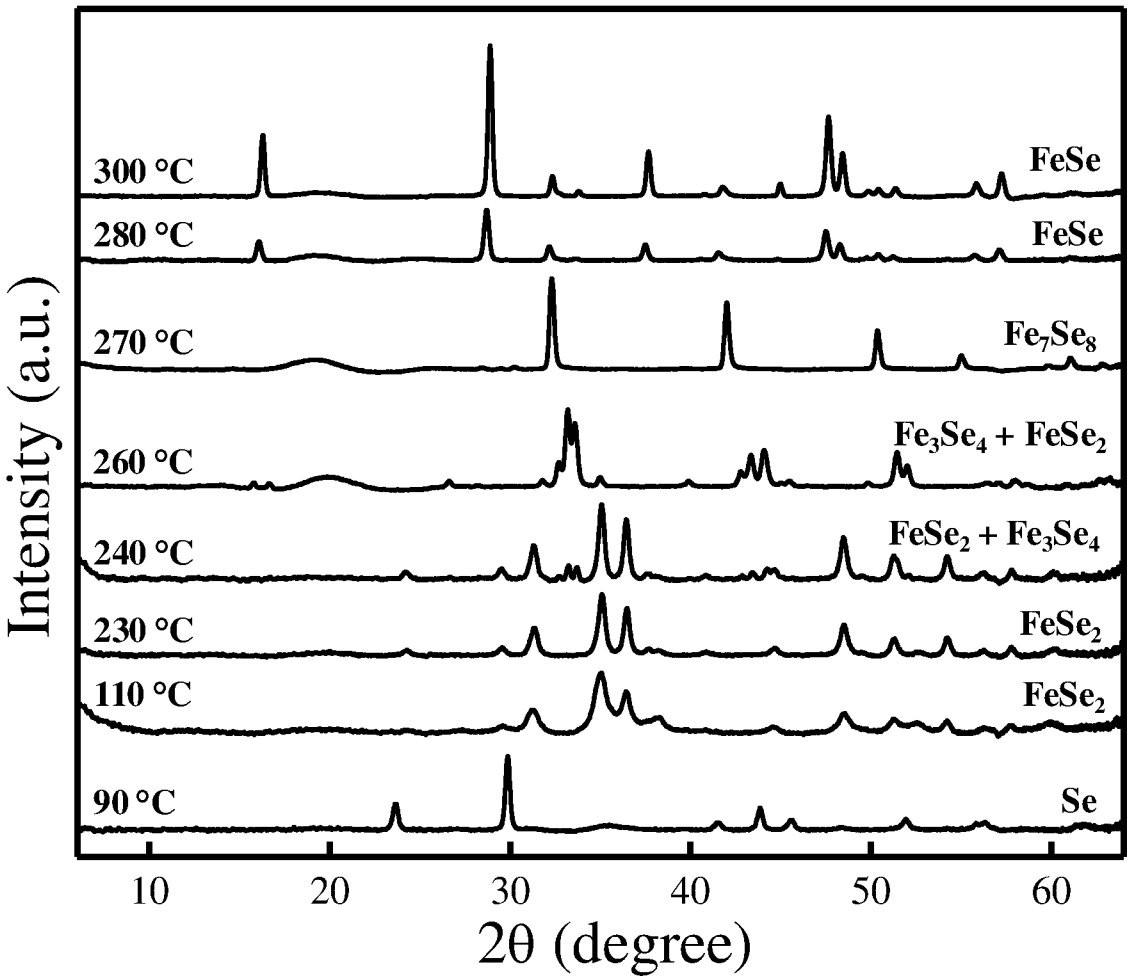
300 °C
FeSe
280 °C
FeSe
270 °C
Fe7Se8
260 °C
Fe3Se4 + FeSe2
240 °C
FeSe2 + Fe3Se4
230 °C
FeSe2
110 °C
FeSe2
90 °C
Se
Intensity (a.u.)
10
20
30
40
50
60
2θ (degree)

Figure 2

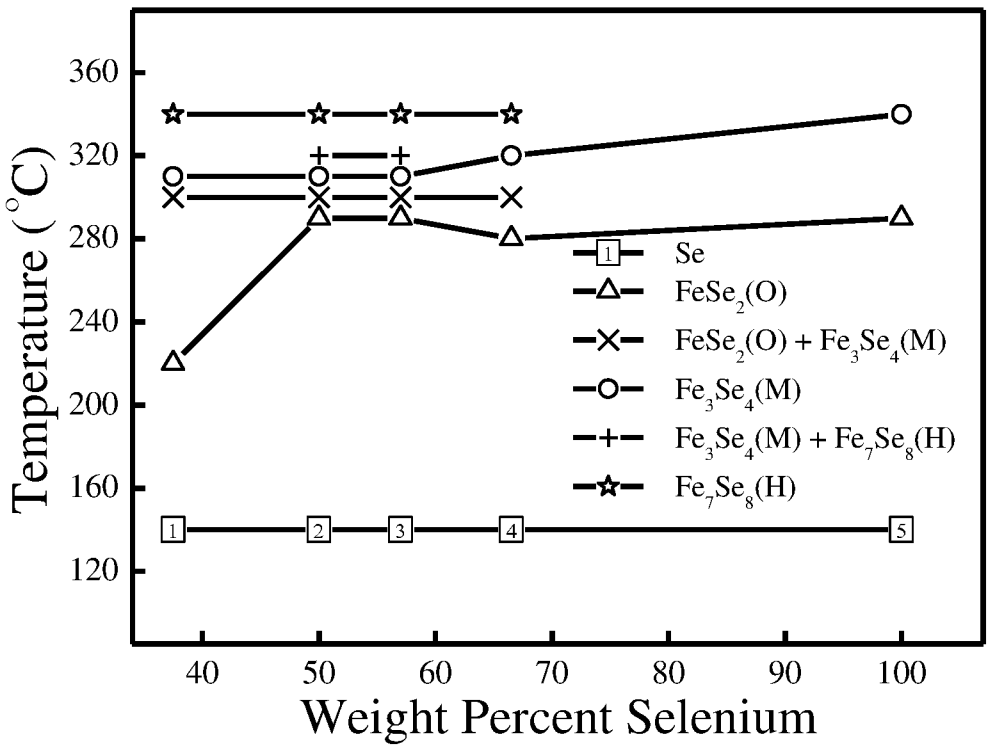
Temperature (°C)
360
320
280
240
200
160
120
40
50
60
70
80
90
100
Weight Percent Selenium
1
2
3
4
5
Se
FeSe2(O)
FeSe2(O) + Fe3Se4(M)
Fe3Se4(M)
Fe3Se4(M) + Fe7Se8(H)
Fe7Se8(H)

Figure 3

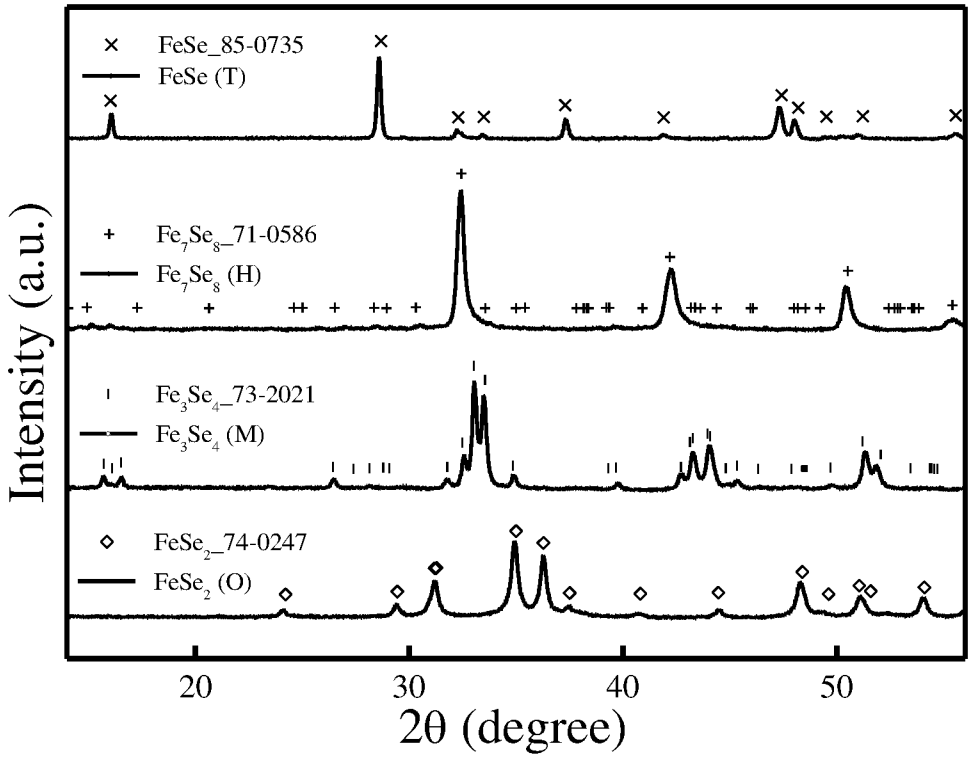
FeSe_85-0735
FeSe (T)
Fe7Se8_71-0586
Fe7Se8 (H)
Fe3Se4_73-2021
Fe3Se4 (M)
FeSe2_74-0247
FeSe2 (O)
Intensity (a.u.)
20
30
40
50
2θ (degree)

Figure 4

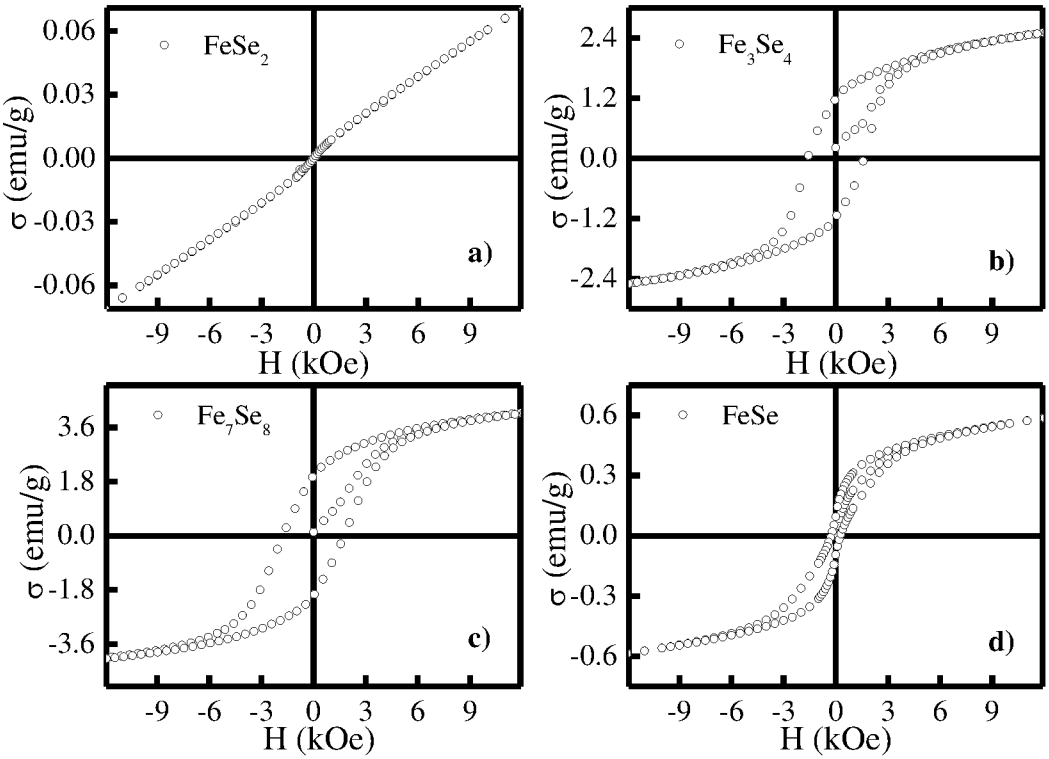

Figure 5

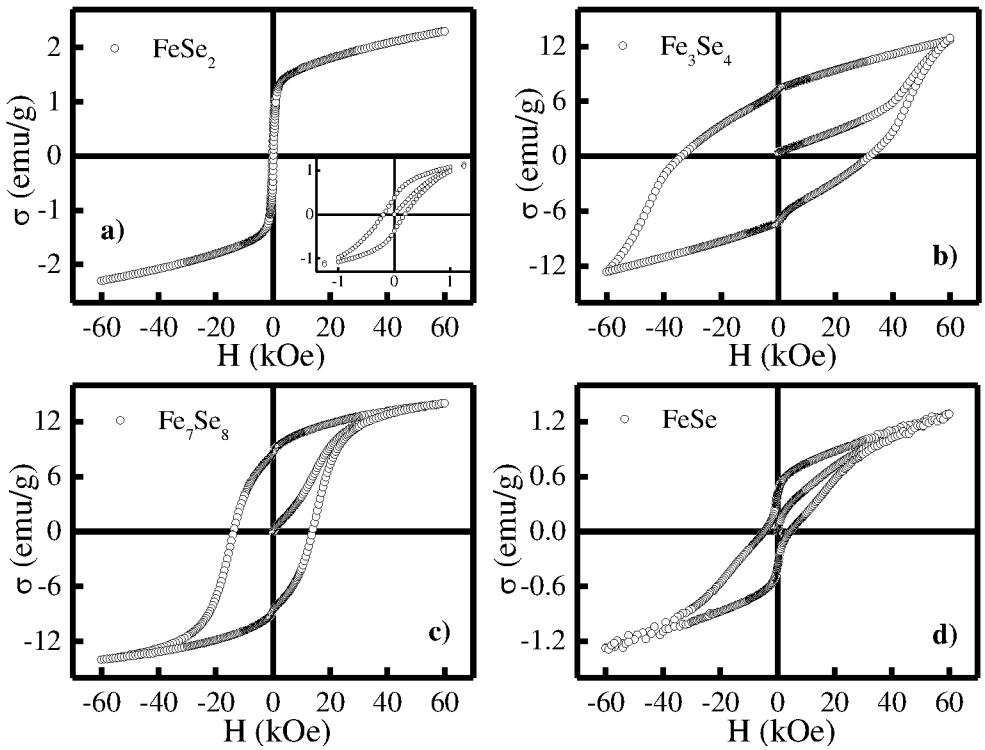

Figure 6

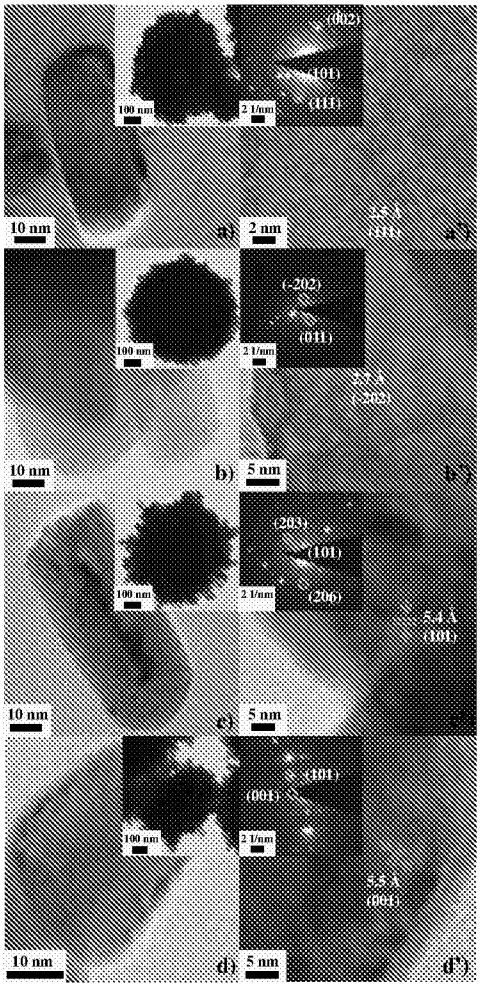
(002)
(101)
(111)
100 nm
2 1/nm
10 nm
a)
2 nm
a')
(-202)
(011)
b)
5 nm
b')
(203)
(101)
(206)
c)
c')
(101)
(001)
d)
d')

Figure 7

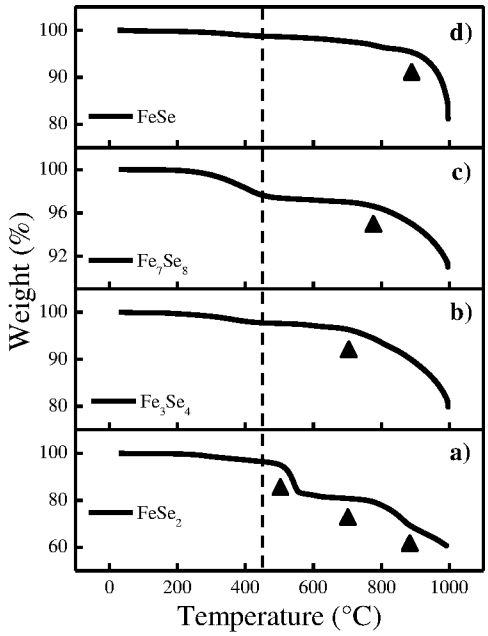

Figure 8

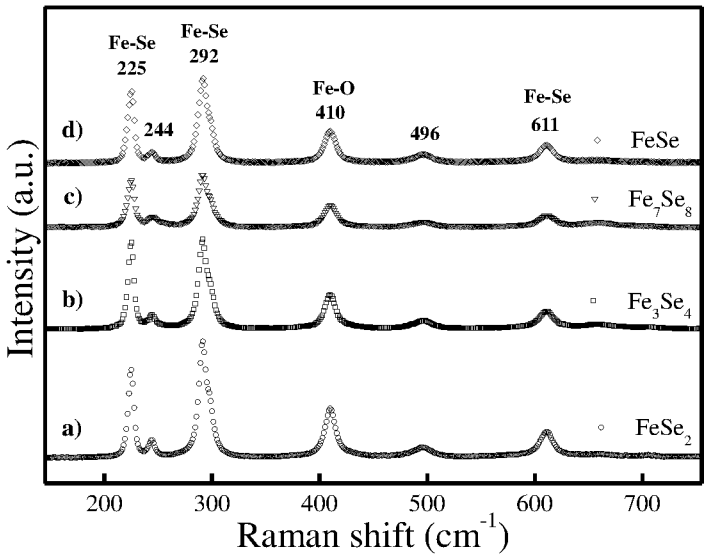

Figure 9

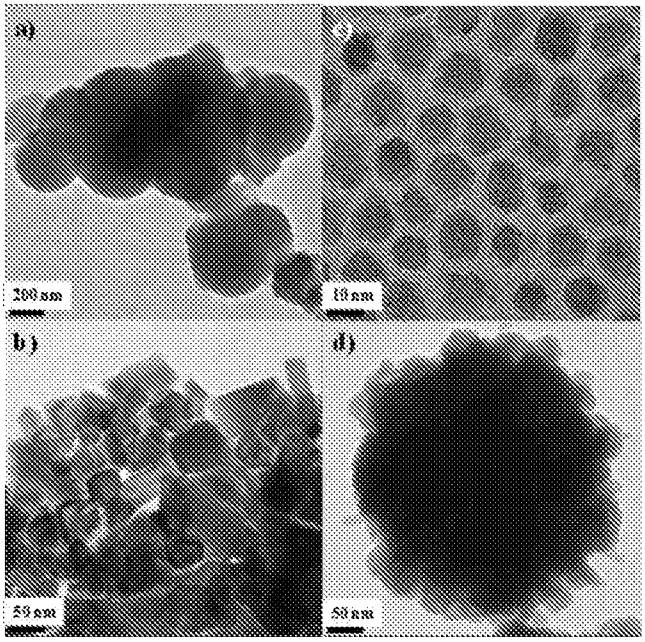

Figure 10

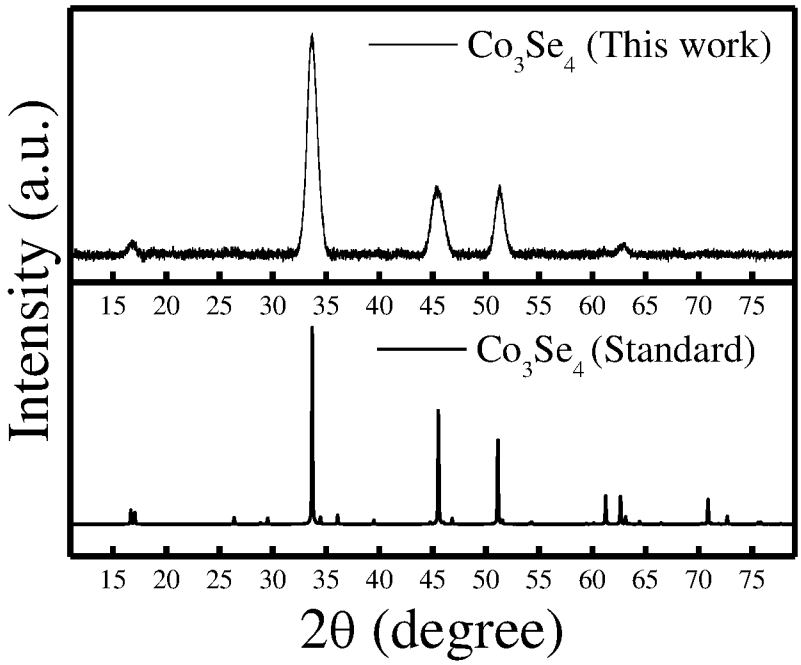

Figure 11

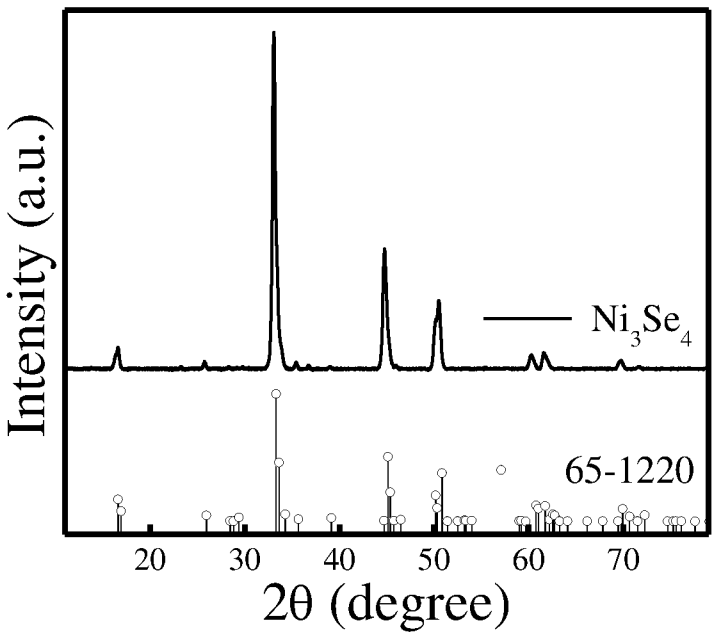

Figure 12

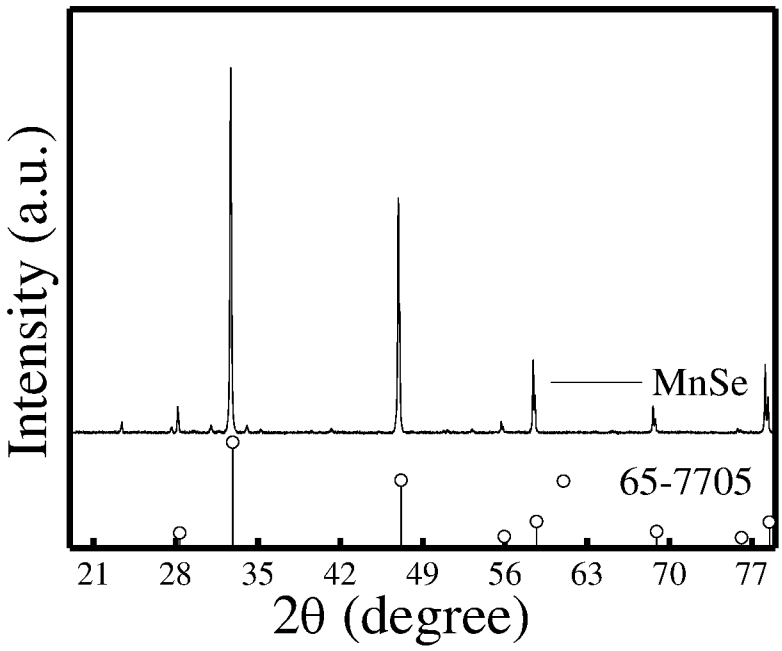

Figure 13

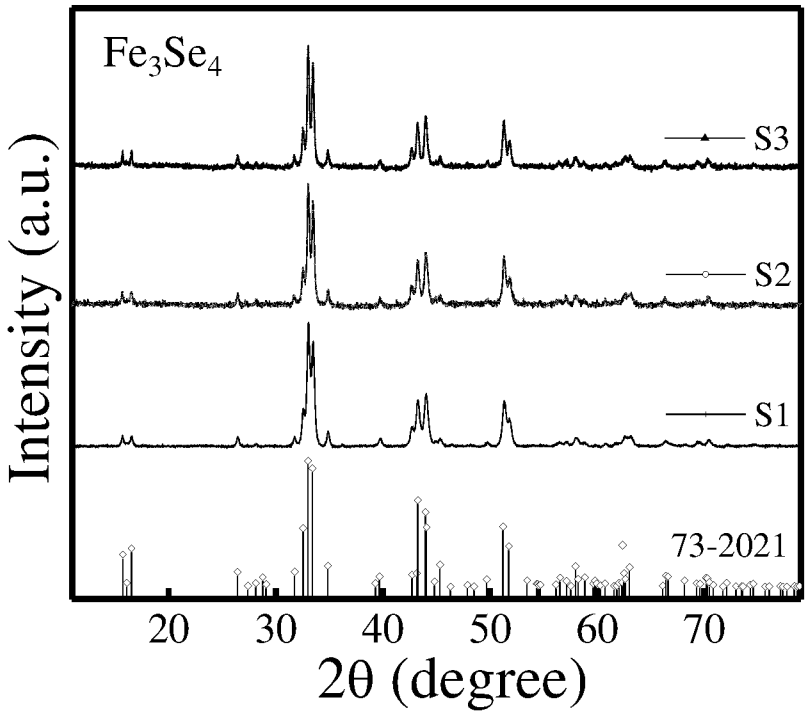

Figure 14

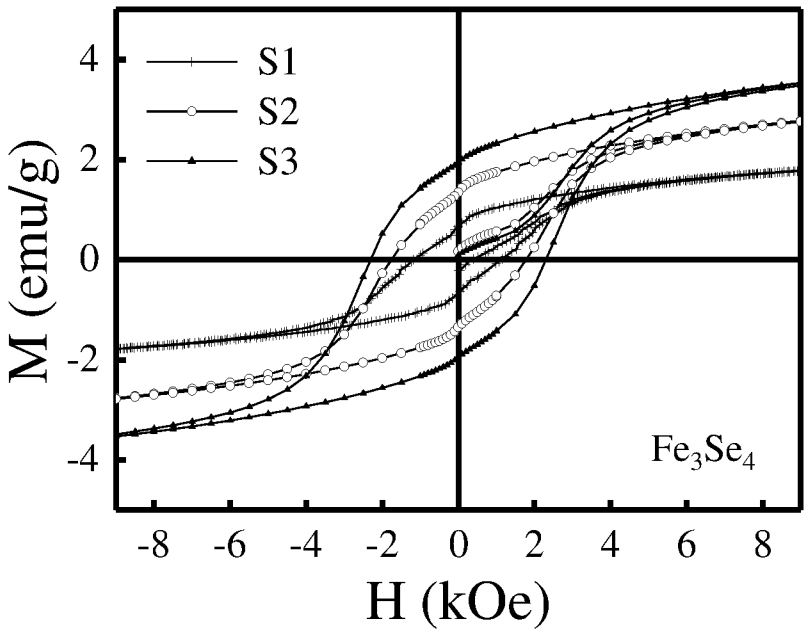

Figure 15

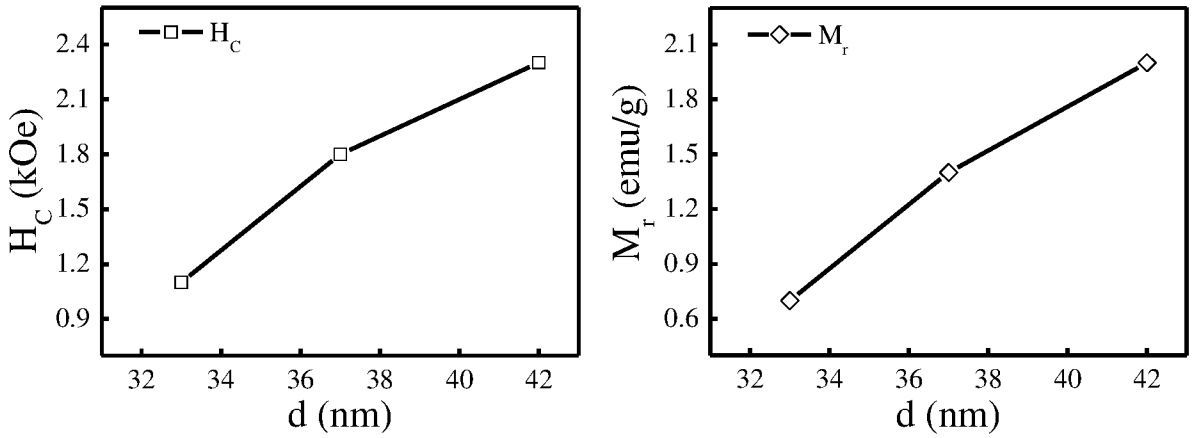
H_C
H_C (kOe)
2.4
2.1
1.8
1.5
1.2
0.9
32
34
36
38
40
42
d (nm)
M_r
M_r (emu/g)
2.1
1.8
1.5
1.2
0.9
0.6
32
34
36
38
40
42
d (nm)

Figure 16

INTERNATIONAL SEARCH REPORT

International application No.
PCT/IN2020/050374

A. CLASSIFICATION OF SUBJECT MATTER
C01G1/12 Version=2020.01

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

C01G

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

TotalPatent One, IPO Internal Database

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	EP 1874686 A2 (YEDA RES & DEV) 09 January 2008 (09/01/2008) Abstract, Claims 1-30	1-10
A	US 2007111319 A1 (CENTRE NATIONAL DE LA RECHERCHE SCIENTIFIQUE) 17 May 2007 (17/05/2007) Claims 1-15	1-10

☐ Further documents are listed in the continuation of Box C. ☒ See patent family annex.

* Special categories of cited documents:
"A" document defining the general state of the art which is not considered to be of particular relevance
"D" document cited by the applicant in the international application
"E" earlier application or patent but published on or after the international filing date
"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
"O" document referring to an oral disclosure, use, exhibition or other means
"P" document published prior to the international filing date but later than the priority date claimed
"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
21-08-2020	21-08-2020
Name and mailing address of the ISA/ Indian Patent Office Plot No.32, Sector 14,Dwarka,New Delhi-110075 Facsimile No.	Authorized officer Amar Nath Tripathi Telephone No. +91-1125300200

INTERNATIONAL SEARCH REPORT
Information on patent family members

International application No.
PCT/IN2020/050374

Citation	Pub.Date	Family	Pub.Date
EP 1874686 A2	09-01-2008	US 2008170984 A1	17-07-2008
		WO 2006106517 A2	12-10-2006
US 2007111319 A1	17-05-2007	EP 1689680 A2	16-08-2006
		WO 2005056479 A2	23-06-2005