

PREPARATION OF STRONTIUM HEXAFERRITE MAGNETS FROM CELESTITE AND BLUE DUST BY MECHANOCHEMICAL ROUTE

R.K.Tiwary*, S.P.Narayan**and O.P.Pandey*

*School of Physics and Materials Science, Thapar University, Patiala- 147 004, India

**Advanced Materials and Process Research Institute (Regional Research Laboratory),
Bhopal 462 026, India

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Abstract

In the present investigation celestite (natural ore of strontium) and blue dust (iron ore fines) have been used for the preparation of strontium hexaferrite powder. The mechanical alloying process has been adopted to prepare strontium hexaferrite powder. The celestite after chemical upgradation and physically upgraded blue dust alongwith sodium carbonate was taken for the preparation of strontium hexaferrite in this experiment. The high-energy planetary ball mill with tungsten carbide jar and ball was used to prepare strontium hexaferrite powder. A long time of ball milling for different duration has led to displacement solid-state reaction. At the end of each experiment the product was washed thoroughly and dried. The X-ray diffraction study after annealing shows the development of single-phase strontium hexaferrite after 40 hrs. of milling. The resultant powder was compacted under magnetic field and sintered to prepare the magnet after annealing the ferrite powder. The magnetic properties were measured by Pulse magneto meter. The moderate value of coercivity, remanence and energy product were observed in this sintered magnet. The work illustrates the feasibility to prepare strontium hexaferrite magnetic powders directly from natural ores which can reduce the total cost of production as compared to conventional method.

Keywords: celestite; blue dust; mechanochemical alloying; magnetic properties

1. Introduction

Blue dust is iron ore fines and is found abundantly in the iron ore mines. It cannot be

used directly in steel making process due to the fineness of the particle. Celestite is natural ore of strontium and is used for the preparation of strontium carbonate.

* Corresponding author: oppandey@tiet.ac.in

Strontium hexaferrite is permanent magnet and its formula is $(MFe_{12}O_{19})$ where M stands for Sr, Ba, Pb etc. Its crystal structure is hexagonal magneto plumbite sometimes called M-type ferrite, which is characterized by space group $P6_3/mmc$ (Krik- othmer, 1993). It is most widely used permanent magnet, which accounts about 90 wt% of total production of permanent magnets market. Strontium hexaferrite finds its application in motors, loudspeakers, high frequency devices, magnetic recording media etc. [2,3].

Generally strontium hexaferrite ($SrFe_{12}O_{19}$) is prepared by the conventional method, which involves calcination of the mixture of $SrCO_3$ and Fe_2O_3 in an appropriate ratio at a temperature between 1100-1200°C followed by sintering [4]. The most important factor for the production of $SrFe_{12}O_{19}$ is the cost and availability of the raw materials. Some researchers have tried to reduce the processing cost by using one of the natural raw materials directly. Mortaza Mozaffari et al. [5], have used celestite along with iron oxide to prepare strontium hexaferrite by mechanochemical method. However, they have taken Fe_2O_3 in pure form. Dasgupta et al. [6], used blue dust with pure strontium carbonate for the preparation of strontium hexaferrite by conventional calcination method.

The aim of the present work is to produce strontium hexaferrite powder directly from celestite and blue dust which are natural ore of strontium and iron by mechanochemical method with a view to make the process cost effective and to explore the possibility of commercial production of strontium hexaferrite directly from the ores. This will

also help to utilize the waste and discarded fines that are causing environmental problem.

2. Experimental Procedure

The starting raw materials taken for this study are celestite, blue dust and sodium carbonate. The celestite ore was obtained from Trichirrapalli district of Tamil Nadu (India), which was supplied by M/s J.M. Mines & Minerals, 37, Williams Road, Cantonment, Tamil Nadu (India). The ore was ground to fine powder in a mortar and pestle. The powder was sieved. The fraction less than 45 micron was collected for the experimental work. The chemical analysis of celestite and blue dust was carried out to know its chemical composition. For different trace elements analysis, atomic absorption spectrometer (flame type model no. GBC-932AA, Australia) was used.

2.1 Chemical treatment of celestite ore

Celestite was chemically treated to remove gangue materials. For it 100 gm celestite powder ($<45\mu m$) was taken in 2 liter borosilicate glass beaker. About 500 ml of 1:1 HCl, 20 ml conc. HNO_3 and small amount of NH_4F was added in this fine powder mass. All acids and other chemicals were of laboratory grade purity. The beaker containing acid and celestite was heated on a hotplate at 60°C temperature with constant stirring for long duration (36 hours). The acid portion was decanted and fresh HCl (1:1) was added followed by small amount of HNO_3 addition to repeat this process. Acid treated celestite was filtered and washed many times with distilled water till the pH of

residue on the filter paper attains neutral value. The filter paper with residue was dried in an oven at 110°C for 2 hours. By addition of HCl and HNO₃ the strontium carbonate present with celestite along with Fe, Ca, dissolves and remains in the dissolved condition in the liquid. NH₄F was added to dissociate any silicate materials present in celestite. By chemical treatment process celestite upgradation is performed and acid soluble impurities like Fe, Ca, etc. get reduced significantly. The chemical composition of celestite before and after acid treatment is given in table 1 and 2 respectively.

2.2 Upgradation of Blue dust

Blue dust was collected from Bailadila mines (Chattishgarh state, India). The particle size <35 µm was collected for the upgradation purpose. For it 100 gm of blue dust was taken in a 2 liter beaker. Beaker containing blue dust was heated on a hot plate at 70°C and compressed air was passed in it through indigenously designed glass

nozzle.

This leads to continuous stirring of blue dust particles. After half an hour heating and blowing process the water was discarded. This process was repeated five times to ensure complete removal of water soluble impurities. After final washing the mass was filtered and dried in an oven at 110°C for 1hour. The schematic view of the froth floatation setup for the upgradation of blue dust fine particles is shown in fig.1. The black particles represent the blue dust fines and grey circles the air bubbles.

2.3 Preparation of Strontium hexaferite powder

The appropriate quantity of treated celestite, upgraded blue dust (mole ratio SrO/Fe₂O₃ =5.5) and sodium carbonate with 30% excess amount to stoichiometric ratio was taken. A batch of 50 gm. mixture was mixed using zircon ball and vessel in a high-energy planetary mill (Model Mega pact, Pilamec Ltd. U.K.) in a medium of analytical grade reagent (AR) hexane. After 1 hour of mixing the material was taken out and put into tungsten carbide jar with tungsten carbide balls. The charge to ball ratio was fixed (1:10). Hexane was used as medium for mixing which continued up to 50 hours. At every 10 hours interval sample colour was monitored till the mixture colour turned to black. During initial experimentation hexane was added to get homogenized mass. As the milling proceeds hexane evaporates leaving fine powders. These dried powders undergo impact welding leading to diffusion in each other of the constituent ingredients in solid state. The mixture was taken out after milling. The mixture was characterized with

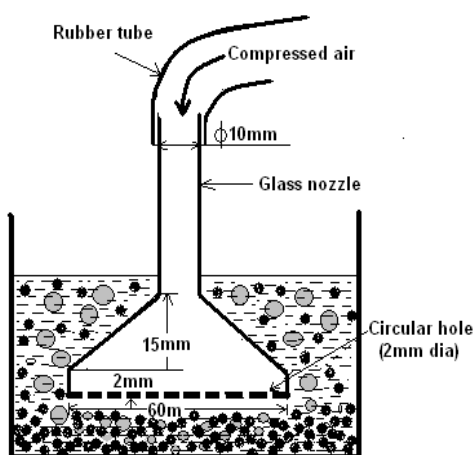


Fig.1. Froth floatation setup for blue dust upgradation

XRD to see the phases present in the product mass. It was observed that formation of ferrite phase does not start in the beginning after 1 hour mixing as can be seen in fig. 2(a). However, distortion in peaks was observed after 30 hrs of ball milling. Finally after 40 to 50 hrs. of ball milling the powder was annealed at 900°C for 1 hour in a muffle furnace to see the presence of phases. Once the phase of strontium hexaferrite after 50 hours of ball milling followed by annealing was confirmed then these powders were selected to prepare strontium hexaferrite sintered magnets. For it 5% PVA (polyvinyl alcohol) as a binder was added to this powder and mixed well to make slurry and was allowed to dry in the open air. The pellet of 5mm diameter and 11 mm length was prepared by applying compressive force of 500 MPa under magnetic field of 2 T to make it anisotropic. The pellet was sintered at 1250°C for an hour in a tubular furnace in open air.

3. Results and Discussion

The celestite powder was chemically treated for its upgradation. The percentage value of different ingredients before and after acid leaching is given in table 1. It was observed that even after acid treatment some impurities like Fe₂O₃, BaSO₄, SiO₂, Al₂O₃ etc. remain in small quantity. The presence of these compounds is not favorable for the magnetic properties of strontium hexaferrite produced there of.

The amount of trace element present in celestite before and after leaching is given in table 2. The chemical analysis and trace analysis of source and upgraded blue dust is given in table 3 and 4.

Table 1. Chemical analysis of celestite before and after acid treatment

| Compound | Before acid leaching (wt %) | After acid leaching (wt %) |
|--------------------------------|-----------------------------|----------------------------|
| SrSO ₄ | 91.60 | 96.66 |
| SrCO ₃ | 1,3 | <0.02 |
| BaSO ₄ | 0.90 | 0.87 |
| Fe ₂ O ₃ | 4,01 | 0.60 |
| SiO ₂ | 0.10 | 0.10 |
| Al ₂ O ₃ | 0.21 | 0.15 |
| CaO | 0.36 | 0.01 |

Table 2. AAS results for other trace elements before and after acid treatment of celestite

| Element | Before acid leaching(wt %) | After acid leaching (wt %) |
|---------|----------------------------|----------------------------|
| Mg | 0.12 | 0.012 |
| Pb | 0.24 | 0.021 |
| Zn | 0.01 | 0.01 |
| Ni | 0.006 | 0.005 |
| Cu | 0.29 | 0.002 |
| K | 0.026 | 0.021 |
| Na | 0.24 | 0.002 |

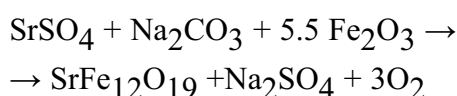
Table 3. Chemical analysis of blue dust before and after upgradation (floatation)

| Compound | Before upgradation (wt %) | After upgradation (wt %) |
|--------------------------------|---------------------------|--------------------------|
| Fe ₂ O ₃ | 96.2 | 97.54 |
| Al ₂ O ₃ | 0.322 | 0.26 |
| SiO ₂ | 1,60 | 1,21 |
| CaO | 0.94 | 0.13 |

Table 4 Trace elemental analysis of blue dust (AAS) before and after upgradation

| Element | Before upgradation (wt %) | After upgradation (wt %) |
|---------|---------------------------|--------------------------|
| Mg | 0.40 | 0.012 |
| Pb | 0.027 | 0.021 |
| Zn | 0.01 | 0.01 |
| Cu | ND | ND |
| K | 0.026 | 0.021 |
| Na | 0.24 | 0.002 |

The reaction involved in milling can be written as:



The characteristic feature of solid-state reaction through mechanical alloying is that it involves the formation of product phases at the interfaces of the reactants [7]. The growth of the product phases occur by diffusion of atoms of the reactant phases through the product phases, which creates a layer preventing further reaction. Intensive milling increases the area of contact between the reactants powder particles due to reduction in particle size which allows fresh surfaces to come into contact [8, 9]. This allows the reaction to proceed without the necessity for diffusion through the product layer due to which solid state reaction that require high temperatures will take place at lower temperature during mechanochemical synthesis without any heat treatment [10]. It is well known that conventional process for the preparation of $\text{SrFe}_{12}\text{O}_{19}$ is through solid-state reaction at high temperature. This requires lot of chemicals of high purity.

Apart from this the requirement for calcination, milling and high sintering temperature makes the process costly. The advantage of mechanical milling, process over other conventional method is that it does not require any external heating source for solid-state reaction to occur [11].

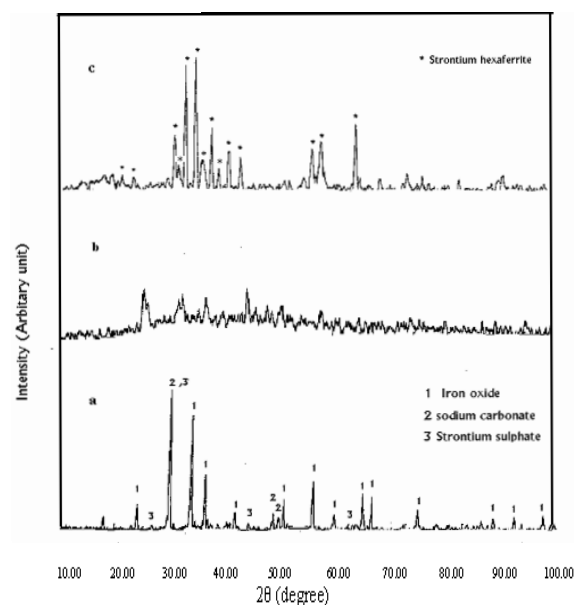


Fig 2. X-ray diffraction pattern of the powders mechanically alloyed for various times (a) after 1 hr. milling (b) after 30 hrs. of milling (c) after 50 hrs. of milling followed by annealing.

3.1 Phase formation

The X-ray study for the formation of strontium hexaferrite ($\text{SrFe}_{12}\text{O}_{19}$) phase is presented in fig.2 (a-c). The XRD pattern after 1 hour of ball milling of the mixture of celestite, sodium carbonate and iron oxide show the presence of all constituent phases which is shown in fig.2 (a). The fig.2 (b) represents the X-ray diffraction pattern of

initial mixture after 30 hrs. of mechanical milling. It indicates the formation of strontium hexaferrite phase. However, presence of ingredient phases also exists. The much weak and broaden peaks of Fe_2O_3 and SrSO_4 are visible with formation of small amount of amorphous $\text{SrFe}_{12}\text{O}_{19}$ phase [12, 13]. The peak broadening of initial oxides indicates that shorter time of mechanical activation is not sufficient to obtain crystalline phase of $\text{SrFe}_{12}\text{O}_{19}$.

However, similar pattern was also observed even for higher mechanical milling time indicating that reaction is not completed. The fig.2 (c) shows the typical XRD pattern after 50 hrs. of mechanical milling followed by annealing at 900°C for 1 hour. Here we can find that there is decrease in amorphization nature. More sharp peaks of $\text{SrFe}_{12}\text{O}_{19}$ are visible in this pattern showing the increased volume of ferrite phase which has formed after 50 hrs. of milling followed by annealing. The X-ray pattern shows the formation of single-phase strontium hexaferrite phase [14]. The particle size of $\text{SrFe}_{12}\text{O}_{19}$ powder after annealing was measured by applying advance Scherer equation. The calculated value of ferrite particle is 17.1 nm. It appears that even after annealing the particles are of nano size which after sintering gets converted to micron size.

The lattice parameter was calculated using following formula.

$$(1/d)^2 = 4/3 [(h^2+hk+k^2)/a^2] + 1^2/c^2$$

where d = inter spacing between planes

hkl = Miller indices

c, a = lattice parameter

The theoretical values of c and a are 23.037 and 5.886 Å whereas calculated values from X-ray diffractogram of these are 23.289 and 5.6613 Å respectively. The observed lattice parameters are close to the theoretical values.

3.2 Magnetic properties

Magnetic properties of ferrite powder produced after different milling time

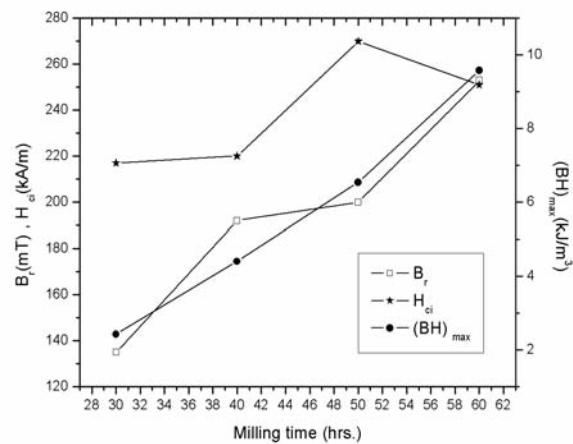


Fig. 3 variation of B_r , H_{ci} with different milling time after annealing and sintering

followed by annealing is shown in figure 3. By increasing the milling time magnetic properties are observed to increase. This is due to increasing volume of strontium hexaferrite phase. This is because of the fact that annealing releases the mechanical stresses existing in powders due to impact load [15]. The typical B-H loop of the sintered anisotropic strontium hexaferrite is shown in fig. 4.

Mortaza Mozaffari et al.[5] have reported the direct utilization of celestite for the preparation of strontium hexaferrite powder using high purity iron oxide after longer time

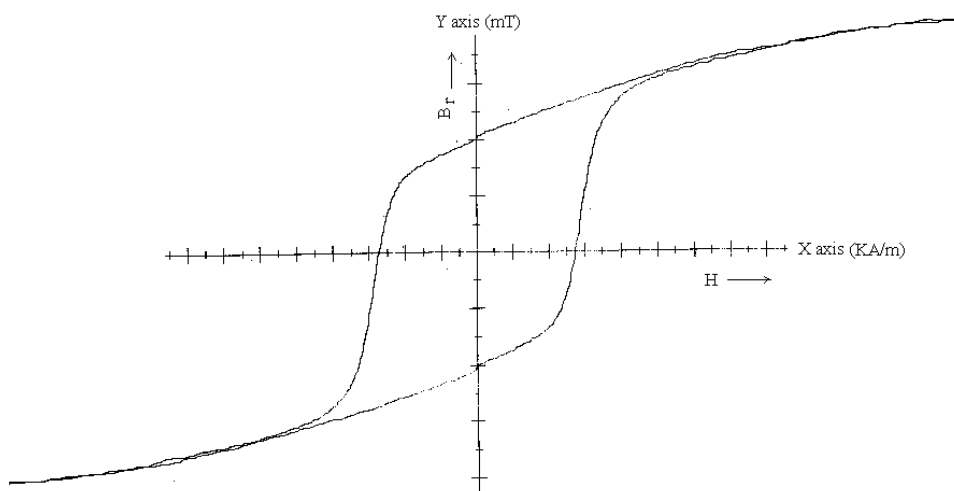


Fig. 4 B-H loop of anisotropic $SrFe_{12}O_{19}$ sintered magnet.

Table 5. Comparison of magnetic properties of strontium hexaferrite by mechanochemical alloying

| Sr.No | Ingredients | Magnetic properties | | | References |
|-------|---|---------------------|---------|------------|-----------------------------|
| | | Br (Gs) | Hci(Oe) | BHmax MGOe | |
| 1 | Celestite, sodium carbonate iron oxide (pure) | 2305 | 5230 | 1.2 | Mortaza Mozaffari et al.[5] |
| 2 | Strontium carbonate (pure), iron oxide (pure) | 2100 | 4600 | 1.85 | C. Miclea et al.[13] |
| 3 | Strontium hexaferrite, iron sulphide | - | 5700 | - | J.Sort et al.[14] |
| 4 | Strontium hexaferrite | 2400 | 4200 | 1.2 | S.V.Ketov et al [15] |
| 5 | Celestite, sodium carbonate blue dust | 2533 | 3160 | 1.19 | Present investigation |

of milling (24 hours). They have employed milling process to achieve intimate mixture of celestite, sodium carbonate and iron oxide. The milled powder was calcined at 1000°C for 10 hours. In their process no mechanochemical reaction has taken place. The product phase (strontium hexaferrite) was obtained after calcination. The magnetic properties of these sintered samples are shown in table 5.

Miclea et al. [12] have produced strontium hexaferrite powder by mechanical alloying method. However, they have used strontium carbonate and iron oxide of high purity. Severe stresses and structural deformation was reported in their work. These stresses were relieved by annealing process. Strontium hexaferrite prepared with high purity raw materials exhibit good magnetic properties (Table 5). The coercivity

is the extrinsic property, which depends mainly on particle size, annealing temperature and packing factor of the material. The single domain size of strontium hexaferrite is about $1\mu\text{m}$ [10]. Due to mechanical alloying particle size has reduced to nano size.

Sort et al. [13] in their experiment tried to improve the coercivity of the strontium hexaferrite by ball milling of pure $\text{SrFe}_{12}\text{O}_{19}$ and FeS. The coercivity enhancement observed is due to the formation of $\alpha\text{-Fe}_2\text{O}_3$ phase which has formed after ball milling (table 5).

S.V.Ketov et al. [14] have made the nanocrystalline $\text{SrFe}_{12}\text{O}_{19}$ powder using high energy milling process from pure strontium hexaferrite powder. This process covers only improvement in magnetic properties by high energy milling and annealing (table 5).

The present study involves the solid-state reaction by mechanochemical reaction using celestite and blue dust. After the reaction the powder was annealed. The magnetic properties show the moderate value of remenence and energy product and the coecivity as shown in table 5.

The chemically upgraded celestite and modified blue dust has been used in the present experiment. Some siliceous impurities are always occluded with iron ore, which in all proportion does not favour the magnetic properties. The celestite even after chemical upgradation is not free from impurities. The lower value of magnetic properties may be attributed due to presence of retained impurities as discussed above. Apart from this the value of sintered density of the magnet obtained in this experiment is 4.9 gm/cc , which is lower than the

theoretical density 5.1 gm/cc [16]. The decrease in density also causes to lower (BH)max value. However, the magnetic properties obtained in the present investigation are within the range of other researchers as given in table 5 where they have used milling process to synthesize strontium hexaferrite [17, 18].

The prolonged milling led to the decrease in the value of Br, Hci and (BH)max due to severe mechanical stresses and by formation of soft magnetic amorphous phase. After annealing the magnetic properties increase significantly due to recrystallisation [19, 20].

3.3 Microstructural Studies

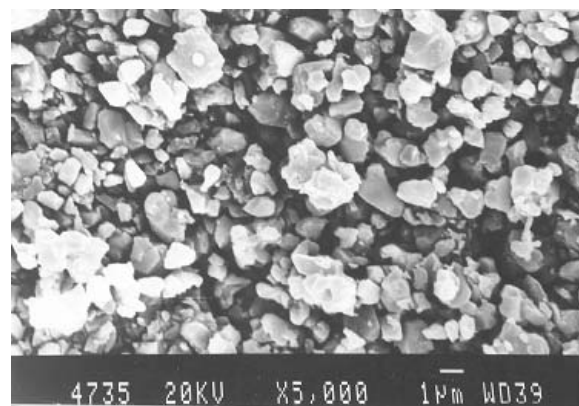


Fig. 5 SEM micrograph of $\text{SrFe}_{12}\text{O}_{19}$ powder after annealing.

Fig. 5 shows the SEM micrograph of strontium hexaferrite annealed powder, which was obtained after gold sputtering. This shows the hexagonal grains of ferrite. Fig. 6 shows SEM micrograph of the fractured surface of the ferrite magnet. The major portion of particles is in range of $1\mu\text{m}$. The grains are elongated showing orientation of ferrite particles. During the process of annealing and sintering small particles of

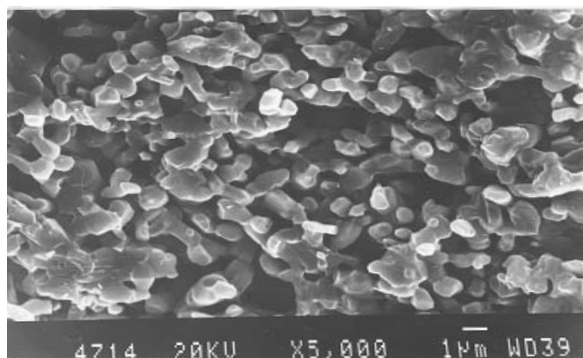


Fig. 6 SEM of fractured surface of sintered $\text{SrFe}_{12}\text{O}_{19}$ magnet.

strontium hexaferrite have grown to single domain $\leq 1 \mu\text{m}$.

4. Conclusion

The result of magnetic properties obtained in the present investigation shows that strontium hexaferrite with moderate values of remanence, coercivity and energy product can be obtained by mechanical alloying of celestite and blue dust followed by annealing. These magnets can be used in those components where moderate magnetic properties are required. The most important features of this work are as follows.

(a) The lower cost of starting raw minerals (celestite and blue dust) will make the process more economical to produce strontium hexaferrite magnets as compared to the other conventional methods where high purity chemicals are utilized.

(b) The mechanochemical method is direct method for the solid-state reaction and this does not require any additional step like conversion of celestite to strontium carbonate and high temperature reaction. Therefore it makes the process easy and

economical.

(c) This innovative process will definitely help to exploit the large deposit of Indian celestite and waste blue dust on commercial scale for their utilization and for the development of strontium hexaferrite, which exhibit moderate magnetic properties and is cost effective.

(d) The values of magnetic properties obtained in present work are within the range of those reported using mechanochemical work as has been compared in table 5.

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