Effect of low sintering temperature on the structural and magnetic properties of M-type strontium hexaferrite

KUSH RANA (✉ kushrana88@gmail.com)

University of Delhi

Research Article

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Abstract

A pure M-type strontium hexaferrite with nominal composition $\text{SrFe}_{12}\text{O}_{19}$ was prepared via modified conventional citrate precursor method. The basic idea of investigation was to improve the quality of hexagonal ferrite without high temperature sintering as these ferrites are generally known for high temperature sintering techniques. Thermogravimetric analysis (TGA/DTA) of powdered sample was carried out to identify the desired crystallization point suitable for the formation of M-phase. After dividing the sample into two equal parts, the prepared sample was sintered at two different temperatures, 800°C and 910°C. The properties of the material were investigated via using important characterization techniques, XRD, FESEM, FTIR, Raman spectroscopy (RS) and VSM respectively. The XRD confirmed the formation of M-phase along with some impurities of Fe_2O_3 and these results were strongly supported via both FTIR and RS. On increasing the sintering temperature, the average crystallite size was found to increase from 25nm to 33nm. The FESEM analysis confirmed the formation of densely packed grains some hexagonal platelets along with agglomerates. The magnetic parameters saturation magnetization (M_s), magnetic coercivity (H_c) and squareness ratio (SQR) were investigated by using VSM. The value of M_s for ferrite sample sintered at 910°C was found to be 92emu/g but at the same time the H_c value was found in the range of few hundreds of Oersted. This kind of behavior was due to the smaller grain size and the presence of impurity phase which was totally against the nature strontium hexaferrite. Such properties of M-type hexagonal ferrite was found very rare and procured to be an excellent candidate for switching devices, recording media, high frequency applications and many more.

1. Introduction

Magnetic materials have their own significance whether in pure or in complex form depending on their physical and chemical properties. If we look around in our surroundings, from small magnetic beads to telephonic devices and from computers to bulky motors, almost in every device magnetic materials are the key component and that's why they are the most imperative part of our life [1]. Magnetic materials, especially magnetoplumbite strontium hexaferrite have been extensively explored due to its ability to retain the magnetization even after the removal of the magnetic field. In present scenario almost more than half of the market worldwide has been captured by these hexaferrite because of their alluring applications in power transmission, electronics appliances, medical equipment's, scientific instruments sensor & actuators and many more [2–3]. Because of numerous applications these multitalented materials are investigated since last seven decades by the scientific community as a material for permanent magnet, future multi-ferroics, high frequency applications and many more [4].

Generally M-type hexagonal ferrites are formed by spinel and hexagonal R, S, R*, S* blocks as a building material possessing P6₃mmc symmetry [5]. Regarding the enhancement of magnetic properties of M-type SrM hexaferrite, their physical properties may require some modification. This can be achieved by altering their morphology and small grain size, which is achieved by using different processing techniques [6–7]. In recent years, several process like co-precipitation, sol-gel, solid state, citrate precursor,

hydrothermal, auto combustion and many more chemical processes has been implemented to improve the crystal structure because magnetic properties are strongly influenced by the crystal structure [8–12]. It has been reported that both pure and substituted barium and strontium hexagonal ferrites with some modification on their processing techniques were employed to achieve higher values of saturation magnetization [13–16]. Some limited reports were also available that supported higher saturation values along with very low coercivity values of the order of few Oersted. This kind of anomalous behavior found in M-type hexagonal ferrites was very rare and found well suitable for recording media such as hard drives and video tapes [17–18].

The main focus of this investigation is to develop a new approach for processing high quality $\text{SrFe}_{12}\text{O}_{19}$ hexaferrite via citrate precursor method without raising the sintering temperature at higher level against the status of hexagonal ferrite. The relationship between the structural, spectroscopic and magnetic properties of prepared hexagonal ferrite was investigated and thoroughly studied.

2. Experimental Procedure

M-type strontium hexaferrite was synthesized via a modified conventional citrate precursor method at low sintering temperature. High purity chemicals of AR grade ferric nitrate nonahydrate (99%), strontium nitrate (99%) and citric acid (98%) were used to synthesize pure M-type $\text{SrFe}_{12}\text{O}_{19}$.

2.1 Preparation of pure M-type strontium hexaferrite

All the nitrates were weighted stoichiometrically and diluted in deionized water separately to make clear solutions. These solutions were added one by one into the 3M solution of citric acid. The mixture was stirred continuously at low heating rate of $20^{\circ}\text{C}/\text{hour}$ until the highly viscous gel was obtained. Generally, this procedure requires a higher temperature of 200°C once the solution reached to its viscous state for ignition but in this method, the specimen was continuously heated at the same rate until the ignition as a self-propagated process took place rather than putting in the furnace. A brown fluffy mass was obtained. The only reason behind this adjustment was to avoid the overheating of ferrite sample which might result in the degradation of the quality as well as the quantity of ferrite samples.

The crystallization point of prepared sample was identified by using thermogravimetric analysis (TGA/DTA). After identifying the sintering temperature, in order to confirm the crystalline phase of synthesized material, types of atomic bond, morphology and magnetic properties certain characterization like XRD, FEEM, FTIR and RS were performed. The magnetic properties of prepared samples were tested by using VSM at room temperature with an applied field of 10kOe.

3. Results And Discussion

TGA-DTA Analysis of SrM powder before annealing

The thermal decomposition behavior of SrM dried sample analyzed by thermogravimetric analysis (TGA) and differential thermal analysis (DTA) graphs are shown in **Fig.1**. There were two endothermic peaks at 200°C & 500°C and two exothermic peaks at 300°C and 530°C were observed. These peaks are responsible for the phase transformation phenomenon in the SrM sample. To analyze the phase transition of SrM hexaferrite, the DTA curve was divided into three regions i.e. Region1 (100°C-305°C), Region2 (305°C-500°C) and Region3 (500°C-800°C). Region1 indicates the removal of water and the nitrate contents from the SrM sample. Region2 confirms the evaporation of several carbon containing compounds along with the remaining crystallized water vapours, whereas the Region3 confirms the formation of oxide from hydroxide, monoferrites and the beginning of hexagonal phase. On the other hand, the TGA shows the continuous weight loss from room temperature to 800°C. Beyond 800°C no such change in the weight loss was observed which again confirmed the starting of crystallization of SrM. Both the curves meet each other at 910°C without showing any endothermic and exothermic peaks or any weight loss [18-19]. Therefore 910°C is confirmed as the temperature SrM phase formation.

XRD analysis of SrM sintered at 800°C and 910°C

The XRD pattern of SrM samples sintered at 800°C and 910°C are shown in **Fig.2**. All the diffracting planes (006), (110), (108), (203), (205), (206), (301), (217), (2011), (220) with (107) and (114) planes as most prominent plane demonstrates the formation of M-phase [20]. Some impurities of hematite (Fe_2O_3) are also observed and found to be decrease as the sintering temperature increases to 910°C. The average crystallite size for both the samples sintered at 800°C and 910°C are 25 nm and 30 nm calculated by well-known Scherer formula. The structural parameters are refined by Rietveld method by using fullprof software. All the important parameters R_{wp} (weighted residual error), S_{GOF} (goodness of fit) and chi square (χ^2) along with cell parameters were calculated and presented in the Table no.1. Both the samples were belonging to the same space group $P6_3/mmc$ (194). All the refined parameters are well matched with the standard SrM pattern and results in the formation of high quality SrM hexaferrite.

In the Rietveld analysis, the refined parameters were scale factor, background parameters, 2θ zero point, lattice constants, profile half width parameters (u , v , w), the mixing parameters of the Pseudo Voigt function (N_A , N_B), occupancy and atomic positions.

FESEM

The morphology and grain size distribution of SrM hexaferrite sintered at 800°C and 910°C were examined by FESEM and shown in the **Fig.3(a)** and **Fig.3(b)**. At 800°C very fine and uniformly distributed particles along with some agglomerates were observed. The tendency of agglomeration of SrM hexaferrite observed in this sample was the direct consequence of smaller and uniform grains as well as enhanced surface energy [21]. The average grain size obtained was approximately 45 nm. As the temperature increased to 910°C, very fine and well packed grains along with some hexagonal platelets were observed. These platelets also confirmed the existence of M-phase. The average grain size obtained

for SrM sintered at 910°C was 50 nm. These results were well matched with the obtained XRD pattern of SrM crystal.

3.4 FTIR spectroscopy

FTIR spectra of SrM sintered 800°C and 910°C are shown in **Fig.4**. The whole spectra were recorded in the range 1000-400 cm^{-1} . The positions of all the absorption bands of samples were similar to the reported data of SrM while their relative intensity varied. The frequency bands in the ranges 550-580 and 430-470 are corresponding to the formation of tetrahedral and octahedral sites confirming the presence of Me-O stretching in ferrites [20]. In the observed pattern, the band positions at 440 cm^{-1} and 547 cm^{-1} confirmed the presence of Fe-O_6 (octahedral) and Fe-O_4 (tetrahedral) stretching vibration [21]. The frequency band at 597 cm^{-1} attributed to the characteristic peak of strong Sr-O, stretching vibration confirmed the formation of M-phase [22-23]. As the sintering temperature increases to 910°C, all the three characteristics peaks were observed at 445 cm^{-1} , 548 cm^{-1} and 600 cm^{-1} . There was a very minimal change in the positions observed but the length of the dip increased very sharply indicates the very strong bond formation in the ferrite samples. Apart from these bands, the dips at 802 cm^{-1} and 866 cm^{-1} were corresponding to the $(\text{NO}_3)^{-2}$ stretching vibration [24].

Raman Spectroscopy

Raman spectroscopy at room temperature for both the samples was carried out to hold up the information extracted from XRD graphs on the M-type strontium hexaferrite sintered at 800°C and 910°C. It is a very powerful and dynamic tool which gives the information of very minute impurities present in the samples by knowing the position of their atom bonds. On the basis of group theory, in the crystal lattice of M-type strontium hexaferrite there are 42 Raman active modes which include 11 A_{1g} , 14 E_{1g} and 17 E_{2g} [25]. **Fig.5** shows the Raman spectra of SrM sintered at 800°C and 910°C. The peaks observed at 171 cm^{-1} , 310 cm^{-1} , 407 cm^{-1} , 503 cm^{-1} , 610 cm^{-1} and 675 cm^{-1} confirmed the presence of Raman active modes. The peak present at 171 cm^{-1} gives the evidence of the whole spinel block with E_{1g} symmetry [26]. The strongest peak observed at 675 cm^{-1} confirmed the presence of A_{1g} mode representing the presence of trigonal bipyramidal site (2b) whereas the second strongest peak at 310 cm^{-1} represent the E_{2g} mode revealing the mixed octahedral site (2a) [27]. The peaks position at 407 cm^{-1} and 610 cm^{-1} represents the A_{1g} mode with dominating octahedral sites (12k and 4 f_2). These are the five basic modes which ensure the formation of SrM ferrite sample [28]. The peaks observed were well consistent with the magnetoplumbite structure and also found matched with the reported literature [29-30]. Apart from this one peak at 503 cm^{-1} is also observed which confirms the presence of Fe_2O_3 impurity phase [31]. This impurity phase was also confirmed in the XRD pattern. As the sintering temperature rises from 800°C to 910°C, the same modes were observed but differ in the intensity of peaks which confirms the strong Me-O bond formation. This can be attributed due to the increase in the particle size and their homogeneity. Also at higher temperature the presence of impurity phases starts to diminish.

Magnetic properties of SrM hexaferrite sintered at 800°C and 910°C

The hysteresis loops of the M-type strontium hexaferrite ($\text{SrFe}_{12}\text{O}_{19}$) sintered at 800°C and 910°C are shown in **Fig.6**. Some important magnetic parameters like saturation magnetization (M_s), coercivity (H_c), retentivity (M_r) and squareness ratio (SQR) are extracted from these loops and tabulated in Table1. From the M-H loops it is seen that the both the sample doesn't reach its saturation point exactly so the law of approach to saturation (LAS) method has been implemented to calculate the M_s values for each sample shown in **Fig.7**. The equation represent this method is shown as below

$$M = M_s \left\{ 1 - \left(\frac{A}{H} \right) - \left(\frac{B}{H^2} \right) \right\} + \chi_p H \quad 1)$$

Where $\frac{A}{H}$ represent the inhomogeneity of materials, $\frac{B}{H^2}$ represents the magnetic crystalline anisotropy (mca) and $\chi_p H$ the field induced forced magnetization.

So by applying this method to our original data we calculate the M_s Values for SrM sintered at 800°C & 910°C and the values are 80.85 emu/g and 92.19 emu/g. These values are quite higher than the reported M_s values of bulk SrM at low sintering temperatures [32-33]. The reason behind this increase in M_s values can be easily understood from super exchange interaction $\text{Fe}^{3+}\text{-O}^{2-}\text{-Fe}^{3+}$. In the crystal structure of $\text{SrFe}_{12}\text{O}_{19}$, Fe^{3+} ions have been distributed into five interstitial sites. These sites are 2a, 2b, 12k, 4f₁ and 4f₂ respectively. From all these sites, 2a, 12k and 4f₂ belongs to the octahedral site (A-site) having spin up where as 4f₁ belongs to tetrahedral site (B-site) with spin down and 2b belongs to trigonal bipyramidal site with spin up. Net magnetic moment can be calculated by taking the difference between spin up and spin down. So this net magnetic moment will give rise to the super exchange interaction $\text{Fe}^{3+}\text{-O}^{2-}\text{-Fe}^{3+}$ which strongly influenced the magnetization of the materials[34]. From all the five interstitial sites only two sites 12k and 2b are to the ferromagnetic direction due which these site exhibit spin up. Because of this increase in magnetic moment, the super exchange interaction comes to play to enhance the magnetization. From the XRD graph of SrM sintered at 800°C in fig.2 some impurity peaks of Fe_2O_3 have been depicted. With increase in the sintering temperature to 910°C, these peaks intensity are found to be in decreasing order. This decrease in the content of Fe_2O_3 will increase the amount of Fe^{3+} ions which further expands the region of super exchange interaction. Hence the interaction between Fe^{3+} and O^{2-} give rise to the transfer of magnetic moment to the adjacent cations. Therefore with increase in the net magnetic moment, saturation value increased [35-36].

Apart from getting the higher values of M_s higher at lower sintering temperatures, very interesting results of coercivity are observed. The value of H_c of SrM sintered at 800°C and 910°C were 107.90 Oe and 262.92 Oe respectively. The prepared samples reflect the soft magnetic behavior of SrM hexaferrite. This kind of behavior is only acceptable if the particles of smaller size are shifted from multidomains to

single domain [5]. Very few reports are available which shows such kind of behavior of SrM hexaferrite and claimed that this reduction of coercivity value of the order of few hundred of Oe is due to the smaller particle size and non-magnetic impurities present in SrM structure[17-18].

4. Conclusion

M-type Strontium hexaferrite was successfully synthesized by modified citrate precursor method at low sintering temperature. The low sintering temperature was confirmed by the thermal analysis. XRD confirmed the formation of M-phase along with some impurities of Fe_2O_3 which were reduced to some extent for the SrM sample sintered at 910°C . Both FTIR and Raman spectroscopy confirmed the presence of hematite as well as M-phase and well supported the results obtained from XRD analysis. Densely packed hexagonal grains with some agglomerations were observed for the SrM sintered at 910°C . From the magnetic measurement very large value of saturation magnetization 92 emu/g was observed and found to be quite higher than the bulk value. Apart from large saturation magnetization very low value of coercivity i.e. below 300Oe was observed. Such type of behavior observed in M-type $\text{SrFe}_{12}\text{O}_{19}$ was very rare. From the magnetic study, it was concluded that smaller grain size and the strong magnetic interactions between the occupied sites may be responsible for the presence of soft character in such type of hard magnetic materials.

Declarations

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Tables

Table 1 Average crystallite size, lattice constants and Rietveld parameters of SrM hexaferrite sintered at 800°C and 910°C.

Sr. No.	Sintering Temperature (°C)	Average Crystallite size (nm)	Lattice Constant		R Factors		
			a (Å)	c (Å)	R _{wp} %	GOF	χ ²
1)	800	27	5.871	23.108	15.78	1.4	1.91
2)	910	34	5.868	23.305	13.20	1.3	1.68

Table 2 Magnetic properties of SrM hexaferrite sintered at 800°C and 910°C.

Sr. No.	Sintering Temperature (°C)	Magnetization M _s (emu/g)	Magnetic Remanence M _r (emu/g)	Coercivity H _c (Oe)	Squareness Ratio SQR(M _r /M _s)
1)	800	80.85	21.45	107.90	0.26
2)	910	92.19	49.48	262.92	0.54

Figures

Figure 1

TGA/DTA curves of SrM before the sample undergo the heat treatments.

Figure 2

XRD pattern of SrM sintered at 800°C and 910°C along with their Rietveld Refinement.

Figure 3

(a) FESEM micrograph of SrM sintered at 800°C. (b) FESEM micrograph of SrM sintered at 910°C.

Figure 4

FTIR spectrum of SrM sintered at 800°C and 910°C.

Figure 5

Raman spectra of SrM sintered at 800°C and 910°C.

Figure 6

M-H loops of SrM sintered at 800°C and 910°C.

Figure 7

law of approach of saturation (LAS) fitting for calculating saturation magnetization.