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Synthesis of chemically coprecipitated hexagonal strontium-ferrite and its characterization

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Highly uniform submicrometre size particles of hexagonal strontium ferrite ($SrFe_{12}O_{19}$) have been synthesized by chemical coprecipitation technique at pH $\simeq$ 13. Chemical coprecipitation technique has helped in bringing down the ferritization temperature from 1300 to 925° C which is revealed by DTA–TG and XRD studies. Reproducible uniform single domain particle size and its distribution has been observed by scanning electron microscopy. X-ray and Mossbauer studies have identified single phase ferrite with Fe^{3+} ions occupying the proper crystallographic sites. The performance parameters of the sintered isotropic strontium ferrite magnets have proved to be superior by about 20% over the ferrites prepared by conventional ceramic technique.

1. Introduction

Synthesis of strontium ferrite by chemical coprecipitation technique is a continuation of our work at NCL on soft and hard ferrites to improve their performance parameters. We have developed a new method to prepare high-permeability Mn–Zn ferrites used in the telecommunication industry by using stabilized MnO [1, 2]. Stabilization of MnO has been useful in the synthesis of stoichiometric Mn–Mg ferrites [3] which are widely used as square loop ferrites in electronic industries. In the field of hard ferrites, preparation of barium ferrite at a much lower temperature of about 600° C has been possible by liquid mix technique (LMT) using citrate precursors [4]. Recently we have reported strontium ferrite synthesis by coprecipitation having high energy product, $(BH)_{max} = 1.5$ MGOe on isotropic sintered strontium ferrite [5]. New chemical routes followed in the synthesis of high performance ceramic materials are coprecipitation, sol–gel, lyophilized gel, sol precipitation, decomposition of organometallic precursors and spray pyrolysis [6–14]. The major advantages of these techniques over the conventional ceramic method are as follows (i) uniform submicrometer sized particles of high surface area are easily obtained. This results in their high reactivity and subsequent low temperature processing to yield a better material in terms of performance parameters. (ii) Chemical homogeneity on an atomic scale can be obtained by starting with well mixed solutions. (iii) Convenient shaping of articles using low temperature casting methods becomes possible. (iv) High chemical purity and strain free materials can be obtained by avoiding the grinding ball-milling common to ceramic processes. The process of grinding ball-milling introduces lattice strains that have a detrimental affect on magnetic properties [15]. In view of these advantages, the above methods have been used to process high performance Ba–Sr ferrites and simultaneously intensive research efforts have been made to improve further their characteristic properties. In this paper we report the detailed studies on the synthesis and characterization of strontium ferrite by a chemical coprecipitation method.

2. Experimental details

2.1. Preparation of ferrite powders

2.1.1. Ceramic technique

Commercial grades of α-Fe_2o_3 and $SrCO_3$ were mixed in the appropriate molar ratio of 5.5 : 1 (Fe : Sr = 11 : 1) taking into consideration the expected addition of iron from the stainless steel ball-mill as a contaminant. The mixture was calcined at 1300° C for 30 min. The solid lump was wet-milled with 0.2% boric acid [16] to reduce the particle size to about 1 μm using a steel ball-mill for over 90 h. The sample is referred to hereafter as sample a, and is prepared for the comparative evaluation of the magnetic properties with that of chemically coprecipitated ferrite.

2.1.2. Chemical coprecipitation

Strontium ferrite powder is prepared by taking appropriate quantities of LR grade $FeCl_3.6H_2O$ (SD Fine Chemicals, India) and AR grade $SrCl_2.6H_2O$ (Loba Chemie, India) in the same molar ratio to maintain Fe : Sr = 11 : 1 as that of the ceramic method. These were taken in the form of solutions, $FeCl_3$ 2.64 M and $SrCl_2$ 1.2 M, mixed together and added to the required quantities of AR NaOH and Na_2CO_3 (Loba Chemie, India) solutions at a pH $\geqslant$ 13 with vigorous stirring to precipitate the hydroxides of strontium and iron. The precipitate was immediately washed with distilled water to remove Na^+ and Cl^- ions following the standard procedure of centrifugal filtration. The precipitate was dried in air at about 100° C in an oven,

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then calcined at 925° C to obtain single phase strontium ferrite. Finally, to remove any other phase present, if any, the material was treated with 1 : 1 HCl for 15 min, as it dissolves other phases more easily than strontium ferrite [17]. The material is washed free from Cl^- ions by distilled water and then dried. The sample is referred to hereafter as sample b.

2.1.3. Pressing and sintering

Green pellets of both samples a and b were pressed at a pressure of 2.2 tonnes cm^{-2} after mixing with 1% solution of polyvinyl alcohol (PVA). (B-H) against H loops on green pellets were recorded before they were sintered. The magnetic parameters of green pellets were computed from the loops. The major difference in further processing of sintering was with respect to temperature and time requirements needed to obtain properly sintered shapes. The pellet of sample a was sintered at 1280° C for 90 min and that of b at 1200° C for 2 min.

2.2. Physicochemical characterization

The ferrite materials prepared by two different techniques were characterized for comparative evaluation of their structural, thermal, magnetic and electronic properties. The analytical instruments used for characterization are given below.

2.2.1. DTA-TG-DTG

Netzch STA 409 differential thermal analyser was used to obtain the thermal data on ferritization reaction by ceramic as well as coprecipitation method. The instrument simultaneously plots the results of differential thermal analyser (DTA), thermogravimetric analysis (TGA) and derivative thermogravimetric analysis (DTG) along with the sample temperature (T).

2.2.2. XRD

X-ray diffractograms of the powders calcined at different temperatures were recorded with Philips PW 1730 X-ray generator using CuKα radiation (λ = 0.1542 nm).

2.2.3. SEM

Microstructural studies were made with a Cambridge Stereoscan 150 Scanning electron microscope. Ferrite pellets were coated with silver paste to minimize charging effects.

2.2.4. Mossbauer spectroscopy

Fe^{57} Mossbauer Spectra were recorded with a conventional constant acceleration electromechanical drive coupled to ND 100 multichannel analyser operating in time mode. A 10 mCi Rh : ^{57}Co source was used to record the spectra at room temperature. A metallic iron foil (25 μm thick) was used to calibrate the spectrometer and all isomershifts were measured with respect to that of the metallic iron absorber. The hyperfine (h.f.) interaction parameters were computed using an iterative least squares MOSFIT programme adopted to ICL 1409S Computer.

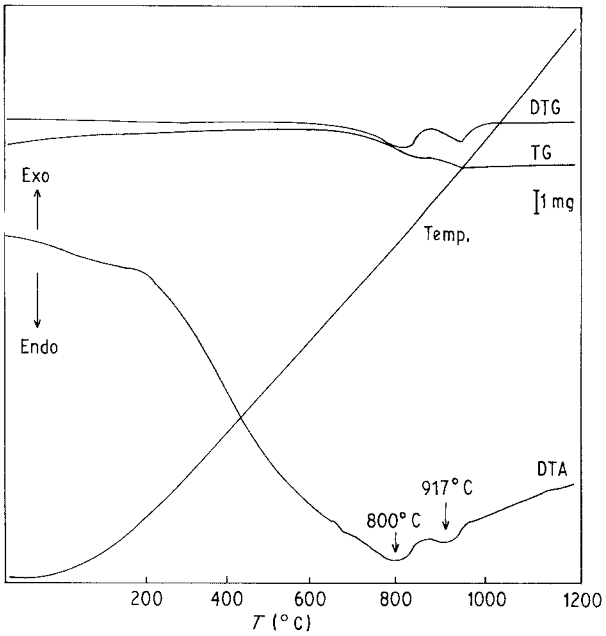

Figure 1 Thermogram of the mixture of α-Fe_2O_3 + $SrCo_3$ in the molar ratio 5.5 : 1

2.2.5. Magnetic measurements

Hysteresis loop – namely magnetic induction (B) against applied magnetic field (H) and (B-H) against H were traced using a hysteresis graph of Walker Scientific Inc., USA model MH 1020.

3. Results and discussion

DTA–TG–DTG plots (Figs 1 and 2) of the mixture of Fe_2O_3 and $SrCO_3$ and the coprecipitate as a function of temperature were analysed to locate the formation of various phases and to establish the ferritization temperature. DTA of the mixture of Fe_2O_3 and $SrCO_3$ shows broad endothermic hump in the temperature range of 800 to 900° C which may be attibuted to the decomposition of strontium carbonate (Strontianite) [18]. Resulting SrO is expected to react with iron oxide

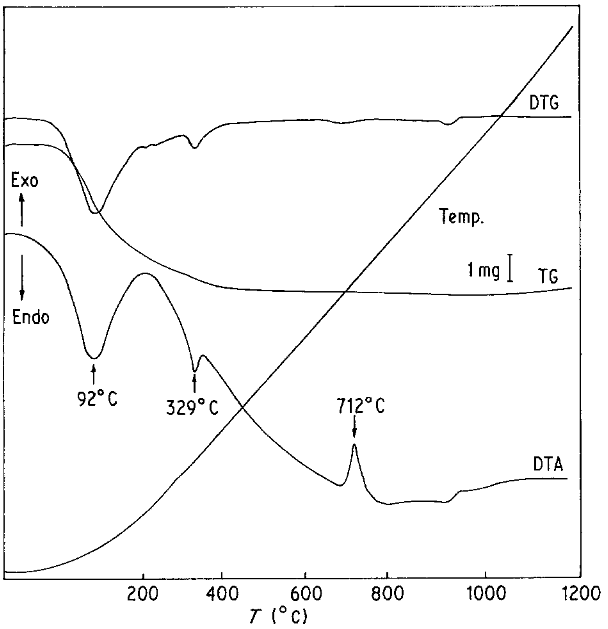

Figure 2 Thermogram of chemically coprecipitated hydroxides of iron and strontium.

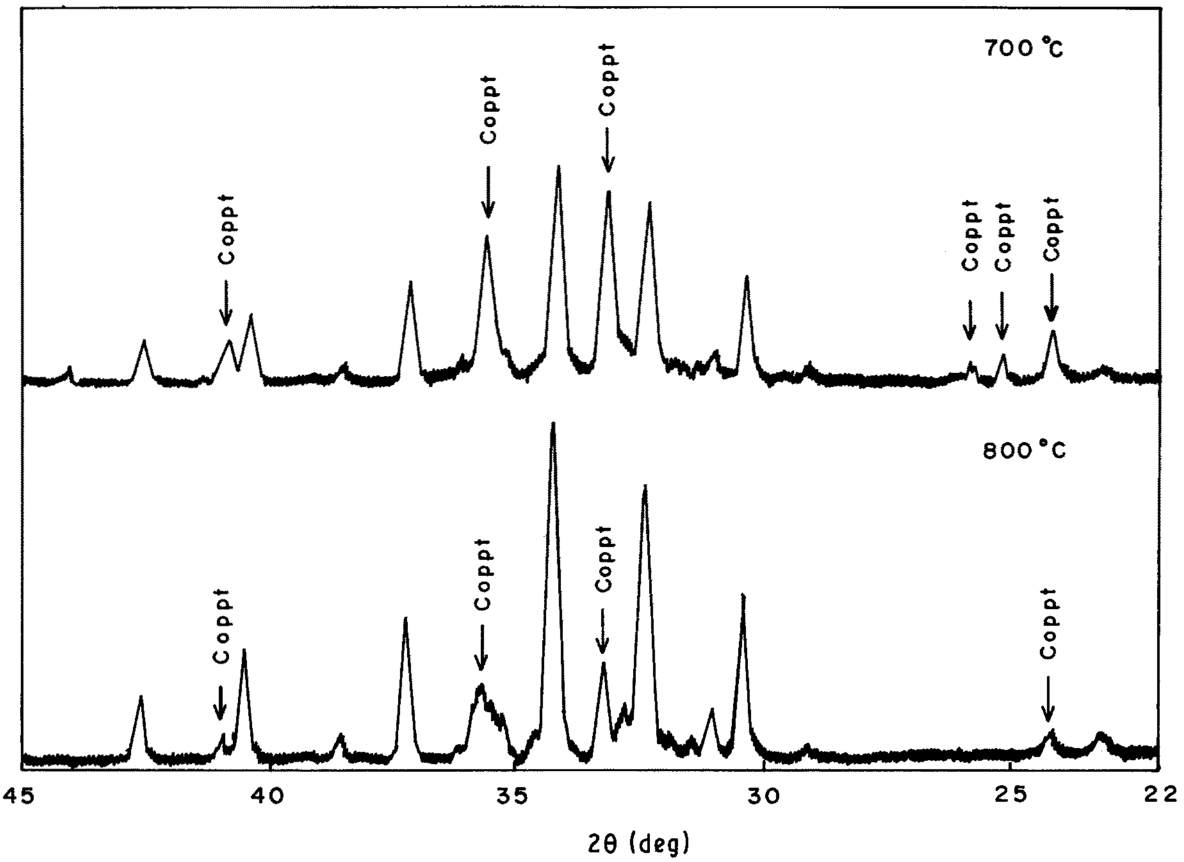

Figure 3 X-ray powder diffraction patterns of the coprecipitate heated at 700° C for 2 h and 800° C for 1 h.

at higher temperature to form strontium ferrite. It was calcined at 1300° C since the DTA does not show an exothermic peak representing the ferritization up to 1200° C (Fig. 1). On the other hand, DTA of the coprecipitate (Fig. 2) shows (i) a large endothermal peak at about 90 to 95° C due to the loss of water, (ii) with increasing temperature, an additional small peak appears at about 330° C which probably indicates further loss of small amounts of water from the mixed hydroxides [19], (iii) at $T = 710°C$, a prominent exothermal DTA peak occurs, indicating a chemical reaction of the precipitate forming the ferrite around 700° C. However, X-ray powder diffraction pattern (Fig. 3) of the coprecipitate heated at 700° C for 2 h showed the presence of substantial amounts of undecomposed coprecipitate along with strontium ferrite formed. Further the formation of the ferrite was incomplete even on heating the coprecipitate at 800° C for 1 h as seen in XRD (Fig. 3). Therefore, the calcination temperature was increased to 925° C for 2 h to complete the formation of strontium ferrite.

TABLE I XRD data of strontium ferrite prepared by two techniques

Coprecipitation technique		Ceramic technique	
d_{obs}	I/I_o	d_{obs}	I/I_o
3.8144	W	3.7824	MW
–	–	3.1078	VW
3.0557	VW	3.0660	W
2.9340	MS	2.9472	MS
2.8732	MW	2.8823	MS
2.8376	W	–	–
2.7526	S	2.7608	S
2.6121	S	2.6195	S
2.5404	MW	–	–
2.5265	MW	2.5334	W
2.4993	MW	2.5060	MW
2.4793	VW	–	–
2.4086	MS	2.4149	MS
2.3305	W	2.3305	W
2.2201	MS	2.2254	MW
2.1404	MW	2.1204	MW

S = Strong, MS = Medium Strong, MW = Medium Weak, W = Weak, VW = Very Weak.

The X-ray powder diffraction patterns (Fig. 4) of the samples a and b show the formation of hexagonal strontium ferrite. The interplanar spacings (*d* values in Table I) match well with those reported by Goto *et al.* [20] confirming the formation of the magnetoplumbite structure.

Scanning electron micrographs of the ceramic (a) and coprecipitated (b) ferrite samples (Fig. 5) show a major difference in the size and distribution of the grains. Sample b shows highly uniform submicrometre size grains ($< 1\,\mu m$) as against non-uniform and bigger grains ranging from 2 to 6 μm of sample a.

^{57}Fe Mossbauer spectra of a and b samples are almost identical except for a small unresolved doublet observed for sample a indicating the presence of unidentified phase. The derived hyperfine interaction parameters are given in Table II. In the magnetoplumbite structure iron ions occur on five different sites [21], the octahedral sites crystallographically known as 2a, 12k and $4f_2$, the tetrahedral sites $4f_1$ and trigonal bipyramid site 2b. Since the Mossbauer spectrum of strontium ferrite distinguishes between four sites (as

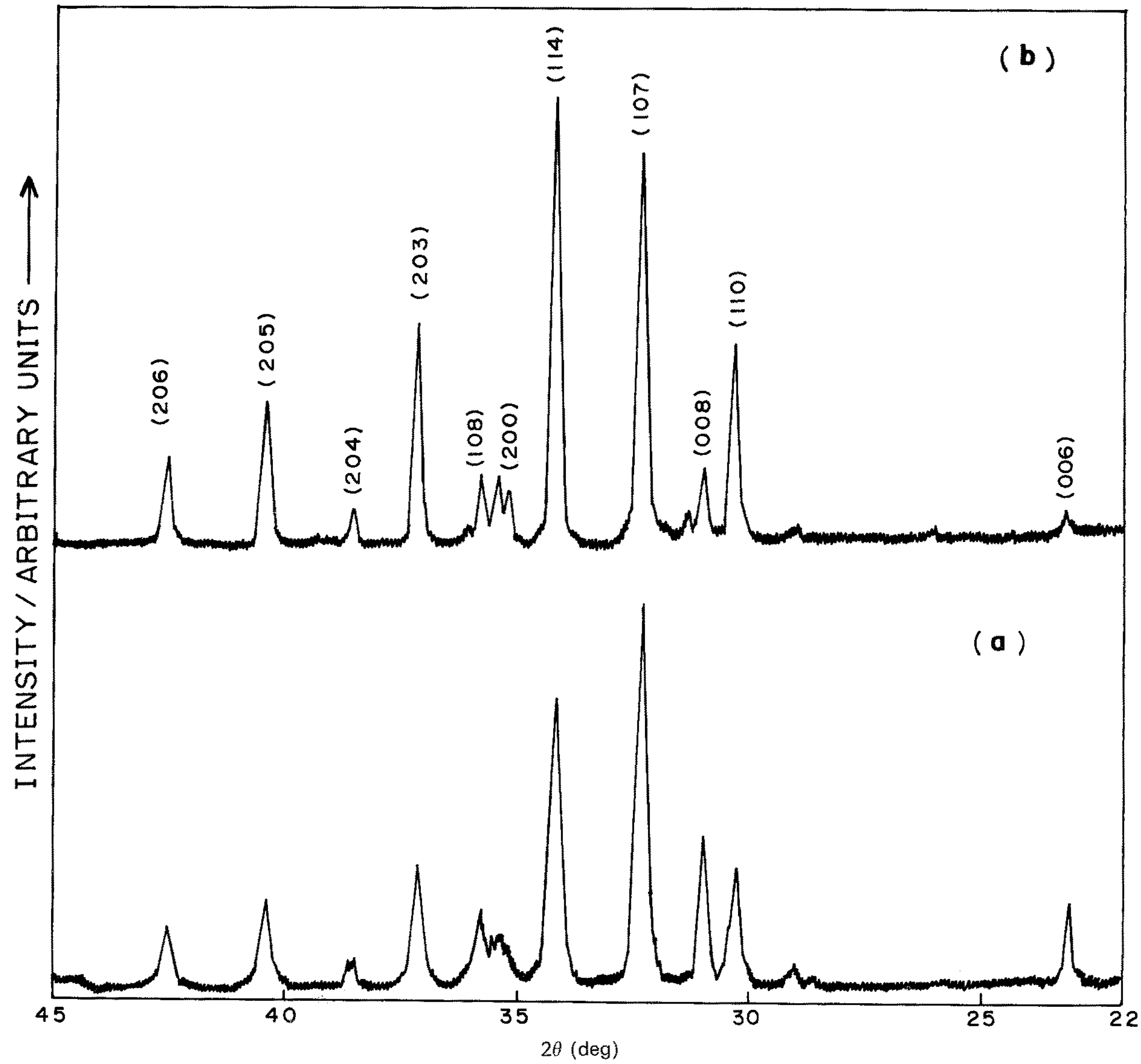

Figure 4 X-ray powder diffraction patterns of Sr-ferrite (a) Ceramic technique, (b) Chemical coprecipitation method.

$4f_1$ and 2a spectra coincide) [22], the hyperfine (h.f.) interaction parameters are given accordingly in Table II. The unidentified phase (very small amount) revealed in the Mossbauer spectrum of ceramic sample may have deteriorating effects on magnetic parameters (Table III). Magnetic induction (B) against applied magnetic field (H) and (B-H) against H loops are plotted on the hysteresis graph for the green (Fig. 6) and sintered samples (Fig. 7).

The shapes of these loops for the two samples are quite different in nature. The magnetic parameters computed from these loops are given in Table III along with the reported best values for strontium ferrite. On comparing the performance parameters of

TABLE II Mossbauer parameters of strontium-ferrite prepared by two techniques

	Coprecipitation technique				Ceramic technique			
Mossbauer parameter	12k	$4f_2$	$4f_1$ + 2a	2b	12k	$4f_2$	$4f_1$ + 2a	2b
Isomershift $\delta \pm 0.02$ mm sec^{-1} w.r.t. Fe	0.37	0.43	0.24	0.42	0.34	0.35	0.31	0.28
Quadrupole splitting $\Delta E \pm 0.02$ mm sec^{-1}	−0.41	−0.20	−0.13	−2.39	−0.41	−0.25	−0.13	−2.38
Hyperfine field $H_n \pm 5$ kOe	414.0	517.0	496.0	419.0	414.0	517.0	496.0	419.0

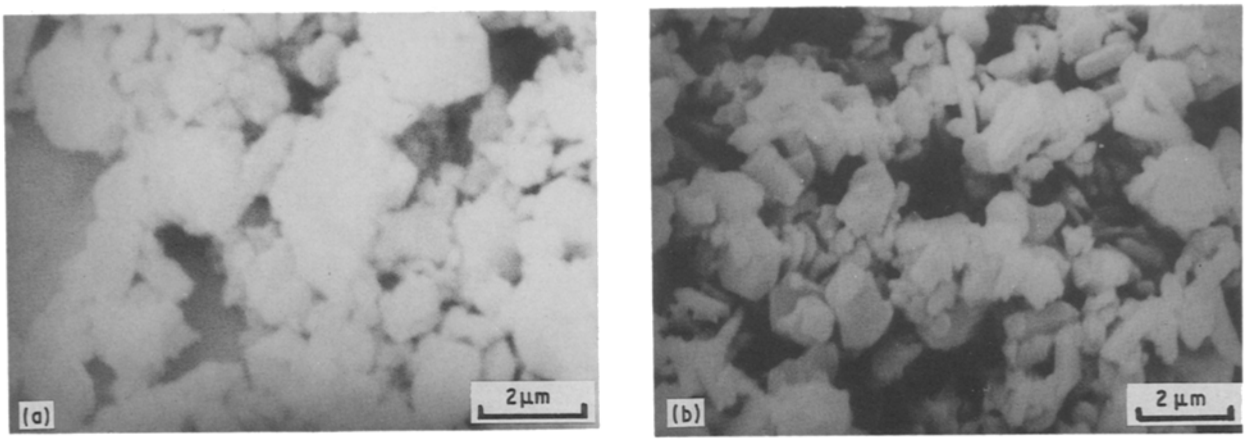

Figure 5 Scanning electron micrographs of Sr-ferrite, (a) Ceramic technique, (b) Chemical coprecipitation method.

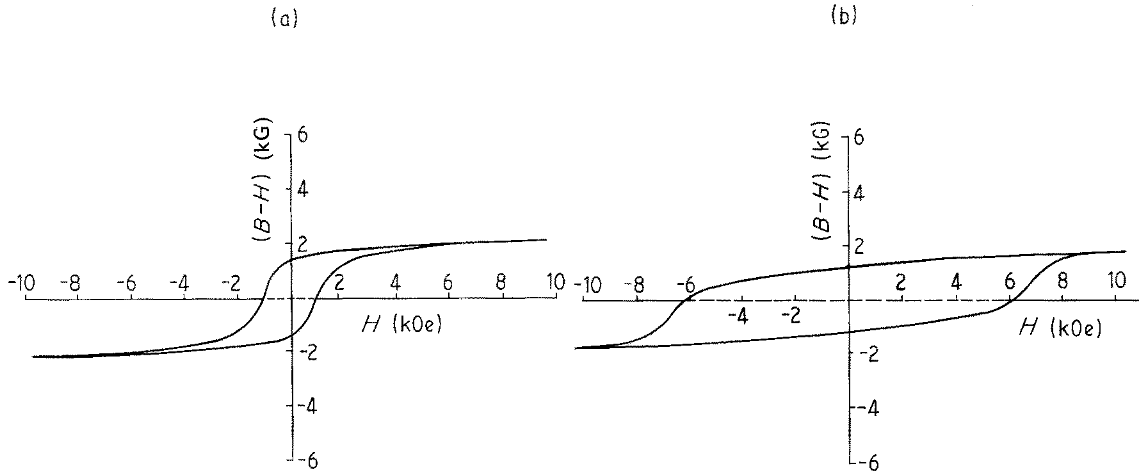

Figure 6 (B-H) against H loops for the green Sr-ferrite (a) Ceramic technique, (b) Chemical coprecipitation method.

the green samples a and b, we observe that the intrinsic coercivity ($_iH_c$) value of sample a is far less than that of sample b indicating the difference in particle size of the two samples. A large value of 6100 Oe for $_iH_c$ has been obtained for the coprecipitated strontium ferrite which is one of the highest recorded for isotropic strontium ferrite by the coprecipitation method [12]. A high value of $_iH_c$ can be attributed to the submicrometer particle size ($< 1\ \mu$m) of the coprecipitated strontium ferrite which is revealed by SEM (Fig. 5b). Performance parameters on sintered ferrite sample a match very well with the reported best values, in fact strontium ferrite a of $(BH)_{max}$ 1.02 MG Oe has got an edge over the reported value of 0.95 MG Oe. Sample b, sintered at a comparatively lower temperature, shows much better properties which is the direct outcome of the method of preparation. The properties of sintered sample b are very close to the reported best values except for $_iH_c$ which is much lower than reported (Table III). This may be due to the increased particle

TABLE III Magnetic parameters on green–sintered isotropic strontium-ferrite prepared by two techniques

Sample	Preparation technique stage	B_r (G)	H_c (Oe)	$_iH_c$ (Oe)	$(BH)_m$ (M G Oe)	D (g cm^{-1})	σ (emu/g)
a	Ceramic–green Cal. 1300° 30min	1400	700	1000	0.28	3.2	52
a	Ceramic/sintered 1280° C for 90 min	2300	1650	2500	1.02	4.7	54
Reported best values on sintered ferrite [23]		2200	1650	2700	0.95	5.0	–
b	Coppt./green Cal. 925°/2 h	1200	1000	6100	0.30	2.9	46
b	Coppt./sint 1200°/2 m	2750	2000	2300	1.65	4.75	53
Reported best value on sintered ferrite [9]		3000	2200	4000	1.70	4.9	60

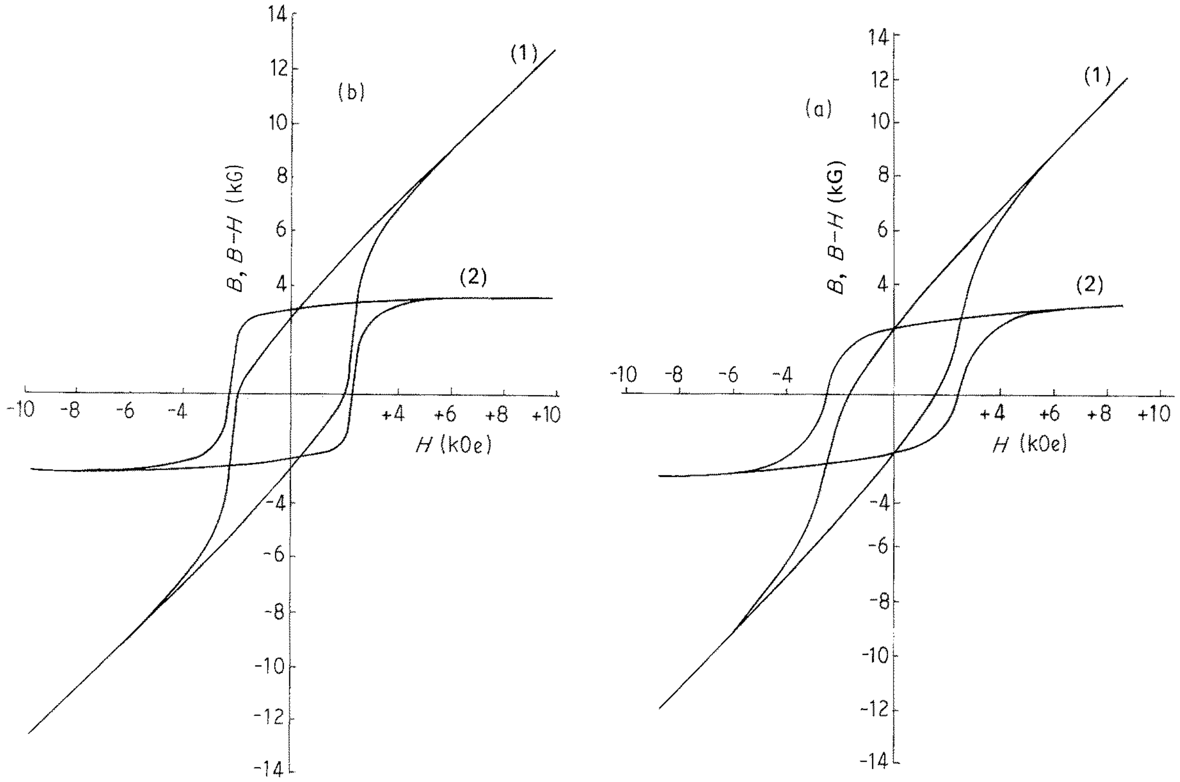

Figure 7 B against H (1) and (B-H) against H (2) loops for the sintered Sr-ferrite (a) Ceramic technique, (b) Chemical coprecipitation method.

size during sintering at 1200°C. Efforts are being made to improve the intrinsic coercivity by sintering at lower temperatures.

Comparative evaluation of these parameters clearly indicates that the chemical coprecipitation route is advantageous in processing high performance ferrite material. Superior magnetic properties such as remanence (B_r), coercivity (H_c), intrinsic coercivity ($_iH_c$), and energy product $(BH)_{max}$ are obtained. Green parameters show a drastic difference in intrinsic coercivity of coprecipitated ferrite as compared to that of ferrite prepared by ceramic technique indicating the difference in their particle size. Performance parameters of the coprecipitated sintered ferrites show superior magnetic properties to the extent of about 20%. Further, the formation of nearly single domain ($< 1\ \mu$m) particles have helped to process these powders at low enough temperatures and have resulted in high performance parameters.

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