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Synthesis of ultra-fine particles of strontium hexaferrite by a modified co-precipitation method

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Abstract

Uniform size and ultra-fine particles of strontium hexaferrite, $SrFe_{12}O_{19}$, with a particle size range from 0.1 to 0.2 μm have been synthesised by what is termed modified co-precipitation from mixed aqueous solutions of iron and strontium nitrates. The results obtained here show that single domain particles of strontium hexaferrite exhibiting a significantly higher coercivity of 444.5 kA/m (5.55 kOe) can be produced by hydrothermally processing a NaOH-precipitated precursor nitrate solution at a lower temperature of 130°C, followed by calcination of the product phase at 850°C for 45 min in air. The effects of the calcination temperature on the phase composition, particle size and shape as well as the magnetic properties of the products have been investigated. It was found that the coercivity increased rapidly on increasing the calcining temperature from 650 to 750°C and then exhibited a maximum at 850°C. The saturation magnetisation increased on increasing the calcination temperature above 650°C. © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: Calcination; Electron microscopy; Ferrites; Hard magnets; Thermal properties

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1. Introduction

Despite the availability of modern permanent magnetic materials with energy products of up to ~12 times higher than those of M-type hexaferrites, these latter magnetic materials remain extremely important and are widely used in numerous technical applications. The principle characteristics and preparation methods of M-type hexaferrites have been reviewed by Kojima[1] and Stäblein,[2] respectively. Strontium hexaferrite $SrFe_{12}O_{19}$ powder can exhibit a high coercivity due to the relatively high magnetocrystalline anisotropy field, making it an attractive material for use in permanent magnet applications.[1] The coercivity is an extrinsic property which is very dependent upon the microstructure. Thus it can be improved by controlling the microstructure, i.e. particle or grain size, shape and size distribution.

Strontium hexaferrite is produced mainly by a conventional mixed oxide ceramic method which involves the calcining of $SrCO_3$ and αFe_2O_3 mixtures at around 1200°C. However, in order to improve the material properties, non-conventional routes such as the co-precipitation method,[3,4] glass crystallisation method,[5] self propagating high temperature synthesis method,[6] and the sol–gel method[7] have also been employed to synthesise strontium hexaferrite. The hydrothermal synthesis of uniform size, high purity strontium hexaferrite particles of plate-like morphology at a relatively low temperature of 220°C held for 1 h has been reported in a previous paper.[8] The process was found to produce ultra-fine particles of intermediate non-ferromagnetic phases with poor magnetic properties when the synthesis temperature was decreased below 160°C.

In the current research, in order to enhance the magnetic properties, particularly the coercivity, the ultra-fine particles of the intermediate phases (which have been synthesised hydrothermally at 130°C) were subjected to calcination at various temperatures.

2. Experimental procedure

An aqueous solution of strontium and iron nitrates (with a Fe^{3+}/Sr^{2+} molar ratio of 8) was co-precipitated

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by the addition of NaOH (aq) to give an OH^-/NO_3^- molar ratio of 2. Subsequently, the precipitated solution was processed in an autoclave at 130°C for 1 h. The details of the synthesis procedure have been described previously.[8] Samples of the resultant powder were then calcined at different temperatures from 650 to 900°C for 45 min in a programmed muffle furnace.

Powder X-ray diffraction (CoK_α radiation) was used for phase identification, while a high resolution scanning electron microscope was used to characterise the particle morphology. The magnetic properties of the powder were determined using a vibrating sample magnetometer (VSM) with a maximum field strength of 1.4 Tesla. The thermal behaviour of the powder sample was evaluated by simultaneous TG/DTA.

3. Results and discussion

Previously, it was found that only particles of the intermediate phases (mainly iron oxide) with poor magnetic properties are produced when the synthesis temperature is decreased to below 160°C during the hydrothermal processing of strontium hexaferrite.[8]

The DTA/TG traces for the sample synthesised hydrothermally at 130°C under the given experimental conditions are shown in Fig. 1. There is an endothermic peak at about 170°C, probably due to the loss of water from the sample, and exothermic peaks at 350 and 733°C. The two exothermic peaks probably correspond respectively, to the conversion of hydroxides to oxides[2] and the formation of strontium hexaferrite. The DTA trace indicates that the strontium hexaferrite can form at a relatively low temperature of 733°C in comparison with that of other wet chemical methods (e.g. compare with 780°C for the sol–gel method).[7] This is probably due to the hydrothermal conditions i.e. the raised temperature and pressure resulting in an accelerated reaction rate.

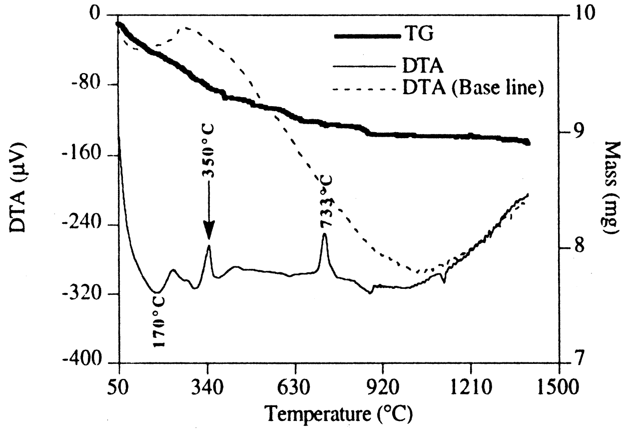

Fig. 1. DTA/TG traces (10°C/min) of the sample synthesised hydrothermally at 130°C for 1 h using OH^-/NO_3^- and Fe^{3+}/Sr^{2+} molar ratios of 2 and 8, respectively.

To aid the analysis and interpretation of the reaction process, the DTA data were supplemented by powder XRD analysis. Fig. 2 shows the powder X-ray diffraction patterns for the samples calcined at various temperatures (i.e. 650, 750, 800, 850 and 900°C) for 45 min in air. Analysis of these patterns confirms that only trace amounts of strontium hexaferrite form at a calcination temperature of 650°C, but the proportion of this phase increases sharply when the calcination temperature increases from 650 to 750°C. Furthermore, as the calcination temperature is increased, there is continued phase transformation from a multiphase to a single phase system; see data in Table 1. Thus the XRD results confirm the reaction sequence attributed to the TG/DTA traces.

From the XRD results that agree with the literature,[9] it may be concluded that, under the given hydrothermal synthesis conditions, the iron nitrate is converted to αFeO(OH), which is then dehydrated to form αFe_2O_3. Subsequently, the strontium nitrate is transformed to

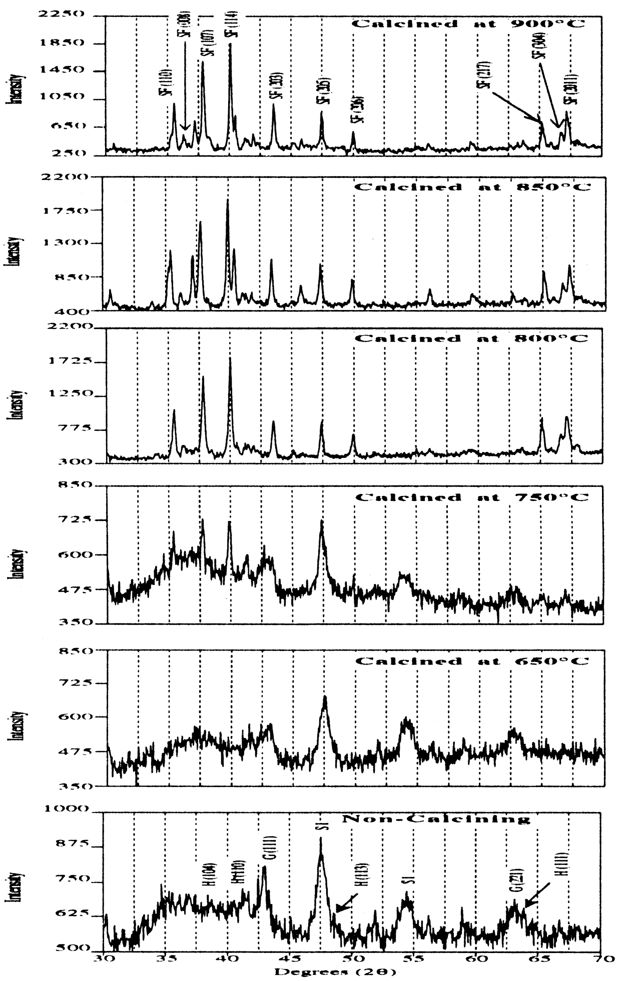

Fig. 2. Powder X-ray diffraction patterns of the calcined samples as a function of calcination temperature (non-calcined sample pattern shown for comparison). SF, H, G and S1 indicate $SrFe_{12}O_{19}$, αFe_2O_3, αFeO(OH) and $SrFeO_{2.5}$, respectively.

mainly $SrFeO_{2.5}$. Finally, strontium hexaferrite is formed during the post synthesis calcination stage. These reaction stages are as below:

Hydrothermal (step 1): $2FeO(OH) \rightarrow \alpha Fe_2O_3 + H_2O$
Hydrothermal (step 2): $Sr(OH)_2 + 6\alpha Fe_2O_3 \rightarrow SrFeO_{2.5} + 5.5\alpha Fe_2O_3 + H_2O$
Calcination: $SrFeO_{2.5} + 5.5\alpha Fe_2O_3 \rightarrow SrO.6Fe_2O_3$

Figs. 3 and 4 are secondary electron imaging (SEI) mode SEM micrographs of the samples calcined at 650 and 900°C, respectively, for 45 min. The sample calcined at 650°C consists of hexagonal particles with an average particle size of 60 nm. The particle size increases from 60 to 145 nm on increasing the calcination temperature from 650 to 850°C, but the particle shape is not changed. After calcination at 900°C, plate-like particles of strontium hexaferrite with an average particle diameter and thickness of 230 and 70 nm respectively, are observed. The mean particle size of this sample is significantly lower than that of the material synthesised hydrothermally at 220°C for 5 h.[8]

The mean particle size of the samples as a function of calcination temperature is shown in Fig. 5. The data reveal that the mean particle size increases with increasing calcination temperature; note the marked inflection in the curve when the calcination temperature exceeds 800°C.

Fig. 6 shows the intrinsic coercivity H_{ci} and saturation magnetisation σ_S of the hydrothermal synthesis products as a function of calcination temperature (see Table 2 for magnetic property data). In comparison with the non-calcined sample, the coercivity of the sample calcined at 650°C increased significantly to 392 kA/m (4.9 kOe) from 60 kA/m (0.75 kOe), while the saturation magnetisation only increased slightly up to 650°C. It appears that the non-calcined sample contains a small quantity of single domain strontium hexaferrite particles (although this phase cannot be identified from the XRD pattern, probably due to it being present at < 10 wt.%), together with a large quantity of non-ferromagnetic material.

The coercivity increased markedly on increasing the calcination temperature from 650 to 750°C, and then

Table 1
XRD determined phase composition of the calcined powder as a function of the calcination temperature

Calcination temperature (°C)	Phase composition
Non-calcined	$\alpha Fe_2O_3 + \alpha FeO(OH) + SrFeO_{2.5}$
650	$\alpha Fe_2O_3 + \alpha FeO(OH) + SrFeO_{2.5}$
750	$SrFe_{12}O_{19} + \alpha Fe_2O_3 + SrFeO_{2.5}$
800	$SrFe_{12}O_{19}$
850	$SrFe_{12}O_{19}$
900	$SrFe_{12}O_{19}$

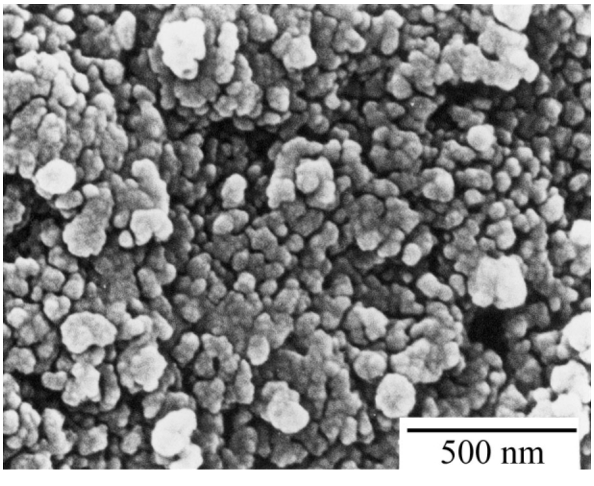

Fig. 3. SEI mode SEM micrograph of the product synthesised by modified co-precipitation under the given experimental conditions and then calcined at 650°C for 45 min in air.

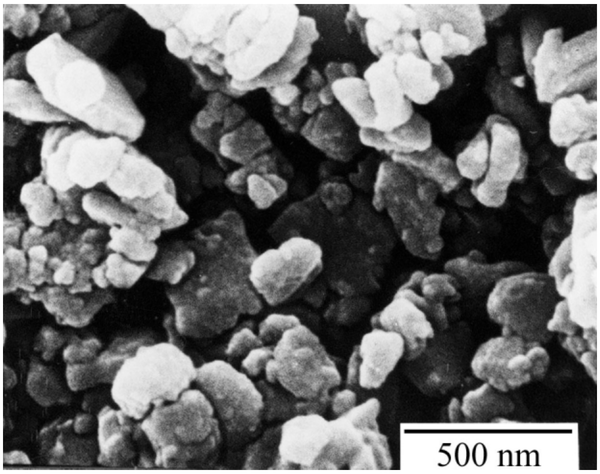

Fig. 4. SEI mode SEM micrograph of the product synthesised by modified co-precipitation under the given experimental conditions and then calcined at 900°C for 45 min in air.

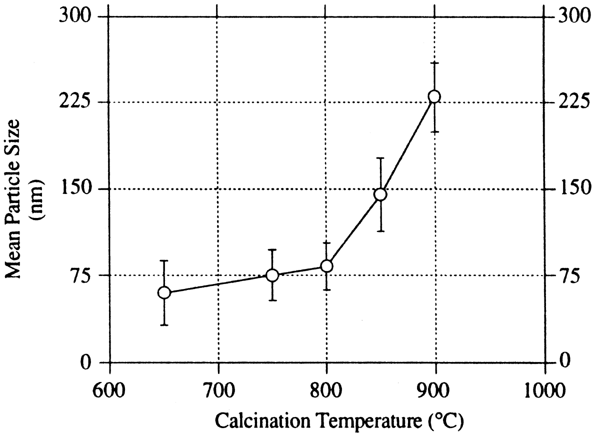

Fig. 5. Mean particle size of the products as a function of calcination temperature. Error bars denote standard deviations.

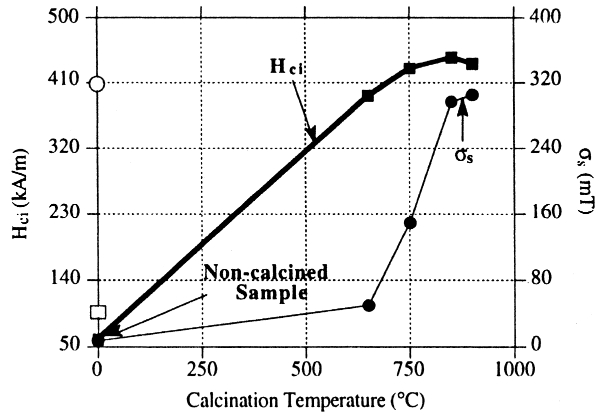

Fig. 6. Intrinsic coercivity H_{ci} and saturation magnetisation σ_S of the products as a function of the calcination temperature. The open square and circle on the *y* axis indicate the coercivity and saturation magnetisation, respectively for a sample synthesised hydrothermally at 220°C for 5 h.

Table 2
Intrinsic coercivity H_{ci} and saturation magnetisation σ_S of the products as a function of the calcination temperature

Calcination temperature (°C)	H_{ci} kA/m (kOe)	σ_S mT (emu/g)
Non-calcined	60 (0.75)	7.7 (1.2)
650	392 (4.9)	49.4 (7.7)
750	429.6 (5.37)	149 (27.9)
850	444.5 (5.55)	296.6 (46.2)
900	436 (5.45)	305 (47.5)

exhibited a maximum at 850°C. An increase in the particle size due to calcination is probably responsible for the decreased coercivity of the sample calcined at 900°C.

The saturation magnetisation increases markedly when the calcination temperature is increased from 650 to 850°C, and then increases very slightly for higher temperatures. The increased saturation magnetisation produced by calcining at temperatures above 650°C is explained by the XRD patterns in Fig. 2 which indicate that the proportion of $SrFe_{12}O_{19}$ phase in the powder is increased.

The results obtained demonstrate that single domain strontium hexaferrite particles exhibiting a very high coercivity of 444.5 kA/m (5.55 kOe) and a saturation magnetisation of 296.6 mT (46.2 emu/g) can be produced by the hydrothermal processing of the precursor nitrates at a low synthesis temperature of 130°C, followed by calcination of the resultant powder at 850°C for 45 min. The presence of some non-magnetic phases which are not detected by XRD could be responsible for a relatively low value of the saturation magnetisation in comparison with that reported in the literature.[3,7] This process is termed modified co-precipitation by the authors because the co-precipitation of the cations from an aqueous precursor solution is completed in the autoclave under hydrothermal conditions.

The strontium hexaferrite particles produced by this method exhibit enhanced coercivity in comparison with the strontium hexaferrite particles synthesised directly as the hexaferrite phase in the autoclave at a higher temperature of 220°C.[8]

4. Conclusion

1. The effects of the post-synthesis calcination temperature on the phase composition, particle size and morphology, as well as the magnetic properties of the intermediate phases, synthesised hydrothermally at the relatively low temperature of 130°C, have been investigated.
2. It has been shown that ultra-fine particles of $SrFe_{12}O_{19}$ with sizes ranging from 50 to 200 nm can be produced by what the authors term the modified co-precipitation method. These powders are believed to consist of single domain particles due to their high coercivity values and the shape of the initial magnetisation curve.
3. The sample synthesised hydrothermally at 130°C exhibited very poor magnetic properties (i.e. coercivity, remanence and saturation magnetisation of 60 kA/m, 0.6 mT and 7.7 mT, respectively). However, these parameters were increased significantly to 444.5 kA/m, 169.5 mT and 296.6 mT, respectively after calcination at 850°C for 45 min in air.
4. The strontium hexaferrite can form at a relatively low temperature of 735°C in comparison with those of other synthesis routes.
5. The results show that the saturation magnetisation of the products is increased on increasing the calcination temperature due to an increase in the proportion of strontium hexaferrite present. However, the coercivity increased significantly on increasing the calcination temperature from 650 to 750°C and then exhibited a maximum at 850°C.

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