

HARD MAGNETIC FERRITES WITH HIGH COERCIVE FIELD

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Abstract

The solid-state reaction between SrCO_3 and $\alpha\text{-FeOOH}$ was investigated by means of thermal analysis, X-ray diffraction, electron microscopy and magnetic measurements. The high reactivity of this mixture is discussed in comparison with that of the mixture of SrCO_3 and $\alpha\text{-Fe}_2\text{O}_3$.

Keywords: acicular particles, strontium hexaferrite

Introduction

In recent years, hard magnetic ferrites characterized by lengthened particles and a high coercive field have found new applications in the manufacturing of magnetic recording media and plastoferrite pieces. This has determined investigations concerning the preparation of materials with chemical formula $\text{Fe}_{12}\text{O}_{19}\text{M}$ ($M = \text{Ba}, \text{Sr}$) by means of solid-state reactions, molten salt reactions and coprecipitation reactions [1-4].

The present paper describes a procedure to prepare strontium hexaferrite by using a topochemical reaction.

Experimental

$\alpha\text{-FeOOH}$ (with a mass loss of 12.26% at 800°C during 2 h, and a specific BET surface of $32 \text{ m}^2 \text{ g}^{-1}$) and $\text{SrCl}_2 \cdot 6\text{H}_2\text{O}$ (reagent grade) were used as raw materials for the synthesis of the strontium hexaferrite.

Stoichiometric amounts were dispersed/dissolved in water during stirring. SrCO_3 was then precipitated on the surface of acicular $\alpha\text{-FeOOH}$ particles by addi-

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tion of an aqueous solution of Na_2CO_3 (13% wt Na_2CO_3) during continuous stirring. The resulting dispersion was heated at 90°C for 2 h during stirring.

After removal of Na^+ by washing with distilled water, filtering and drying at 110°C , the mixture was granulated and submitted to thermal treatment at 1000°C for 2 h in air. During thermal treatment, $\alpha\text{-Fe}_2\text{O}_3$ was generated and then reacted with SrCO_3 to form the strontium hexaferrite.

The thermal behaviour of $\alpha\text{-FeOOH}$, SrCO_3 and their mixture was investigated with a Q-1500 D (MOM, Budapest) derivatograph in the temperature range $25\text{--}1000^\circ\text{C}$, in static air atmosphere, at a heating rate of $10^\circ\text{C min}^{-1}$.

In order to identify the solid crystalline phase, an X-ray diffractometer TUR M-62 was used. The samples were analysed by using CoK_α radiation.

The shapes and sizes of the powder particles were determined through dispersion in distilled water, by means of a TESLA BS-540 electron microscope.

The magnetic properties of the thermally treated powders were determined via an MH/20 Walker-Scientific hysteresisgraph.

Results and discussion

Analysis of the recorded thermal curves reveals that:

– $\alpha\text{-FeOOH}$ undergoes endothermic dehydration in the temperature range $250\text{--}360^\circ\text{C}$, the associated mass loss being about 10%. This result is in fair agreement with that mentioned in the literature [5].

– SrCO_3 undergoes decomposition in the temperature range $930\text{--}1200^\circ\text{C}$. The endothermic peak at 930°C in the DTA curve corresponds to the polymorphic transformation orthorhombic to rhombohedral (Fig. 1). These results are in good agreement with those mentioned in the literature [6].

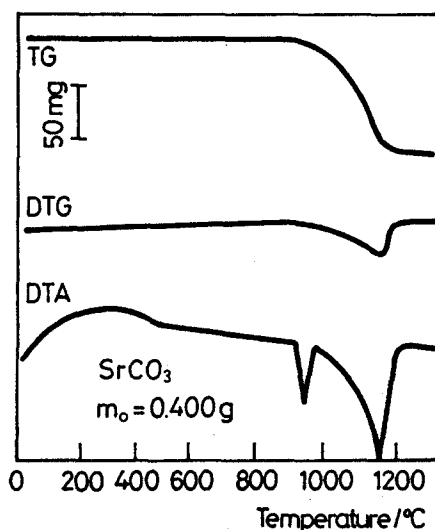


Fig. 1 TG, DTA and DTG curves of SrCO_3

– The thermoanalytical curves corresponding to the mixture $\alpha\text{-FeOOH} + \text{SrCO}_3$ are shown in Fig. 2. The TG curve exhibits a mass loss (8.88% wt) corresponding to the dehydration in the temperature range 70–350°C and decomposition of SrCO_3 in the temperature range 550–870°C (4.41% wt) (Fig. 2).

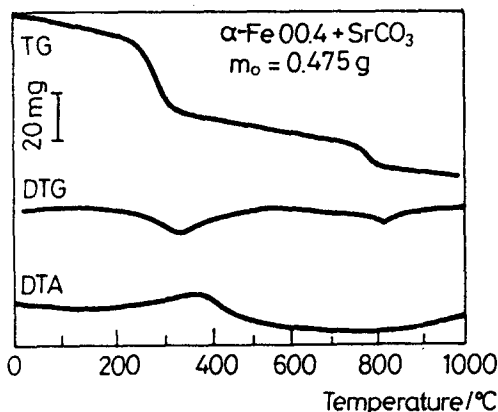


Fig. 2 TG, DTG and DTA curves of the mixture $\alpha\text{-FeOOH} + \text{SrCO}_3$

The temperature range of SrCO_3 decomposition is lower for the reaction mixture than for the phase component. This is probably due to a Hedvall effect [7] induced by the magnetic phase change of the ferric oxide (675°C) [8].

The X-ray diffractograms of the reaction mixture heated for 2 h at 1000°C display lines corresponding to well-crystallized strontium hexaferrite and also to small amounts of SrFeO_{3-x} (Fig. 3a). For comparison, in Fig. 3b the X-ray diffractogram of strontium hexaferrite obtained by the conventional ceramic procedure is shown. The reduced crystallinity of this compound (about 50% with respect to the hexaferrite obtained from $\alpha\text{-FeOOH} + \text{SrCO}_3$), and also the reversal of the intensities corresponding to the (107) and (114) lines, point to unfinished crystallization, even if the chemical reaction is apparently completed.

Table 1 lists the hexagonal unit cell parameters for the strontium ferrite obtained from $\alpha\text{-FeOOH} + \text{SrCO}_3$ in comparison with those for the compound obtained through the conventional ceramic procedure.

Transmission electron microscopy demonstrates the particles of $\alpha\text{-FeOOH}$ to be acicular, with an acicularity ratio of $5 < R < 10$ (Fig. 4a). For particles regarded as cy-

Table 1 Hexagonal unit cell parameters of strontium ferrite samples

Parameters	Strontium ferrite obtained by conventional ceramic procedure (calcined at 1200°C)	Strontium ferrite obtained from $\alpha\text{-FeOOH} + \text{SrCO}_3$ (calcined at 1000°C)
$a/\text{Å}$	5.87	5.87
$c/\text{Å}$	23.02	23.006
$V/\text{Å}^3$	686.60	687.50

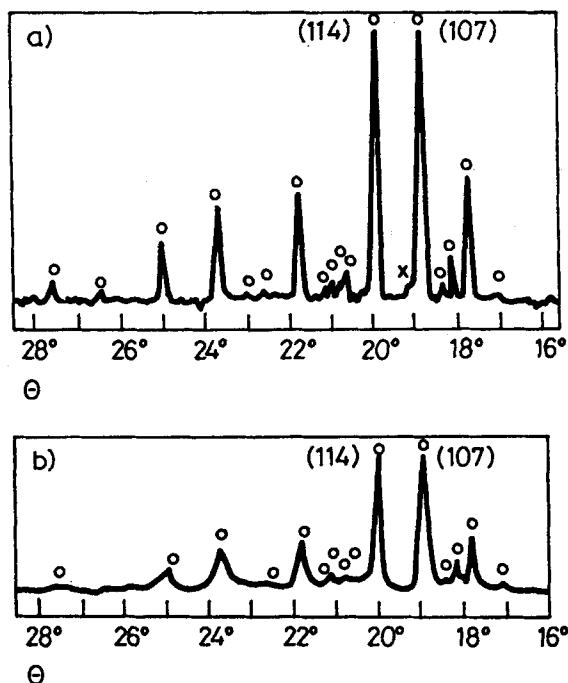


Fig. 3 X-ray diffraction spectra of strontium hexaferrite a) prepared from $\alpha\text{-FeOOH} + \text{SrCO}_3$; b) prepared from $\alpha\text{-Fe}_2\text{O}_3 + \text{SrCO}_3$; o characteristic peak for $\text{SrFe}_{12}\text{O}_{19}$; x characteristic peak for SrFeO_{3-x}

lindrical, R is the ratio of the height L and the diameter d . The precipitate consisting of $\alpha\text{-FeOOH} + \text{SrCO}_3$, washed and dried at 110°C , comprises acicular particles with sizes close to those of the used $\alpha\text{-FeOOH}$ (Fig. 4b). As far as the strontium hexaferrite obtained from the mixture $\alpha\text{-FeOOH} + \text{SrCO}_3$ through heating is concerned, this consists of rod-shaped particles, rounded at the ends, with $0.3 < L(\mu) < 0.5$ and $0.1 < d(\mu) < 0.2$, where L and d are the length and diameter, respectively, of the rods. The slight tendency to sintering of these particles is to be noted (Fig. 4c).

For comparison, Fig. 4d presents the shapes of the particles of strontium hexaferrite obtained by the conventional ceramic procedure, after grinding. Hexagonal crystalline particles (size about 2.5μ) can be seen among smaller particles with irregular shape, coming from the breaking of larger particles.

The acicular shape of the particles was preserved even if the mixture of $\alpha\text{-FeOOH} + \text{SrCO}_3$ was calcined at 1000°C . The morphology of barium hexaferrite powder crystallites obtained from $\alpha\text{-FeOOH}$ and $\text{Ba}(\text{C}_2\text{H}_5\text{O})_2$ is known to change from acicular to platelet on thermal treatment at temperatures higher than 900°C [9].

The magnetic properties (the saturation magnetization, M_s , and the coercive field, jH_c) of the topochemical strontium ferrite powder in comparison with those of the material obtained by the conventional ceramic method are listed in Table 2.

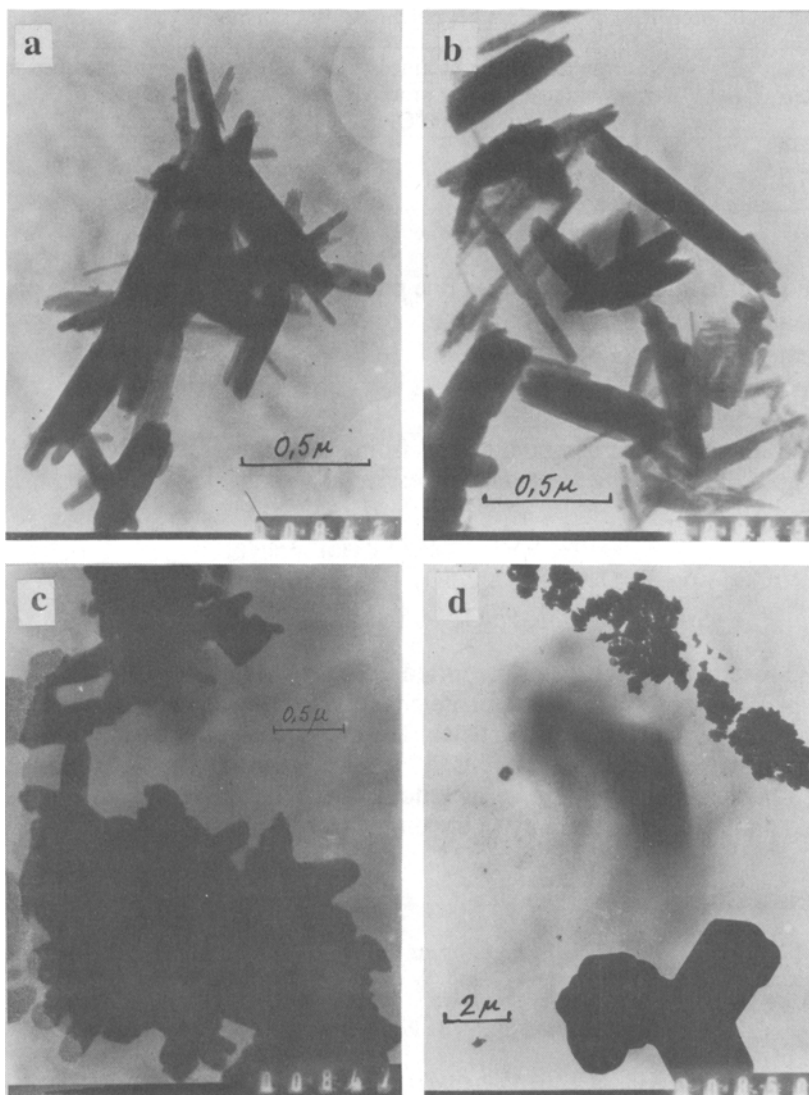


Fig. 4 Microphotograms of particles of a) α -FeOOH, b) mixture of α -FeOOH + SrCO₃, c) strontium hexaferrite from α -FeOOH + SrCO₃, d) strontium hexaferrite from α -Fe₂O₃ + SrCO₃, after wet grinding

These tabulated data indicate that the strontium hexaferrite powder prepared from α -FeOOH + SrCO₃ is characterized by a much higher coercive field than that of the strontium hexaferrite powder prepared from α -Fe₂O₃ + SrCO₃.

This can be explained by:

– the distortion of the crystal lattice as a result of the mechanical milling of strontium hexaferrite from α -Fe₂O₃ + SrCO₃;

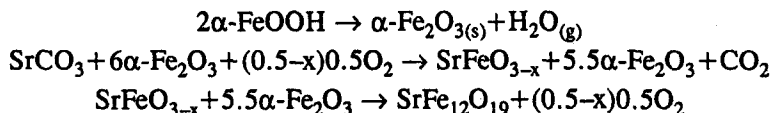
Table 2 Magnetic properties of strontium hexaferrite powder samples

Parameters.	Strontium ferrite obtained by conventional ceramic procedure (calcined at 1200°C)	Strontium ferrite obtained from α -FeOOH + SrCO ₃ (calcined at 1000°C)
$M_s / T \cdot 10^{-4}$	94	103
$H_c / kA m^{-1}$	139.26	368.45

– the regular acicular shape of the fine powder of strontium hexaferrite obtained from the mixture of α -FeOOH + SrCO₃.

Conclusions

Strontium hexaferrite can be obtained from a mixture of α -FeOOH and SrCO₃ according to the following steps on progressive heating:



These results agree with those reported in [1].

The powders of strontium hexaferrite obtained from a mixture of α -FeOOH and SrCO₃ consist of small acicular particles. Thus, their grinding for further use is not necessary (the specific BET surface is 2.7 m² g⁻¹).

The topochemical strontium hexaferrite powder is characterized by a high coercive field and a good dispersivity in organic binders, resins and polymers.

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