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Preparation of barium hexaferrite by a hydrothermal method: structure and magnetic properties

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Barium hexaferrite, $BaFe_{12}O_{19}$, was obtained in hydrothermal conditions from a water suspension of α-FeOOH and $Ba(OH)_2 \cdot 8H_2O$ at a temperature about 315° C. X-ray and Mössbauer spectroscopy as well as electron microscopy investigations demonstrated the appearance of α-Fe_2O_3 as an intermediate phase in the hydrothermal process. The magnetic characteristics of the obtained isotropic magnets are the following: coercive field $H_c \sim 159\,\mathrm{kA\,m^{-1}}$, residual induction $B_r \sim 0.26\,\mathrm{T}$, maximum energy product $(BH)_{max} \sim 12\,\mathrm{kJ\,m^{-3}}$. The hydrothermal procedure for the preparation of barium hexaferrite in comparison with the conventional one is discussed.

1. Introduction

Barium hexaferrite, $BaFe_{12}O_{19}$ (used in ceramic permanent magnets) is prepared conventionally [1] by firing an appropriate mixture of α-Fe_2O_3 with $BaCO_3$ at high temperatures (1150 to 1250° C). The obtained ferrite must be ground in order to reduce the particle size. During or after this process a dry or wet mass is formed, which is pressed and sintered to obtain high-density permanent magnets. The coercive force of these magnetic materials is much less than predicted by theoretical calculations [2, 3]. In addition this procedure requires a large amount of energy (including that used to obtain the raw materials).

In order to remove some of these disadvantages, different methods for the preparation of barium hexaferrite have been proposed [4–8]. Many authors have investigated the system BaO–Fe_2O_3–solvent. By hydrothermal synthesis they succeeded in obtaining some barium–iron magnetic oxides [9–12].

The aim of the present paper is to report the hydrothermal synthesis of barium hexaferrite, its structure and magnetic properties.

2. Experimental procedure

In order to obtain $BaFe_{12}O_{19}$ by hydrothermal processing a water suspension of $Ba(OH)_2 \cdot 8H_2O$ and α-FeOOH was used. The experiments were performed in a 1 l stainless steel vessel (an autoclave). The autoclave was heated at a rate of about 2 to 3° C min^{-1}, kept at temperatures in the range of 260 to 325° C for different times and finally cooled to room temperature. Before the electrical heating the vessel was filled with oxygen to ~8 atm to avoid reduction by hydrogen formed in the reaction between water and the stainless steel vessel. The resulting samples were washed with dilute HCl solution (~0.5M) and then with distilled water until no Ba^{2+} was detected in the liquid. Finally they were dried at about 110° C in air. Many experiments were done to establish the optimum amounts of reactants, the heating rate, and the time and temperature for the thermal treatment.

The products were analysed by means of Mössbauer spectroscopy (Elron type equipment), X-ray spectroscopy (Seifert diffractometer), electron microscopy (Temscan 200 CX) as well as by magnetic measurements (Walker hysteresisgraph). Following the conventional procedure, the hydrothermally synthetized barium hexaferrite was used to obtain permanent magnets.

3. Results and discussion

As is very well known [13] barium hexaferrite, $BaFe_{12}O_{19}$ has the magnetoplumbite structure (hexagonal, $P6_3/mmc$) with cell dimensions $a = 0.5888$ nm and $c = 2.322$ nm (ASTM 7–276). The divalent and trivalent metallic cations are distributed in five inequivalent positions in the lattice [1], 12k, $4f_{IV}$, $4f_{VI}$, 2a and 2b. Consequently the Mössbauer spectrum is a superposition of five sextets [14, 15]. In Fig. 1 the Mössbauer spectrum of barium hexaferrite (obtained by conventional procedures) is shown (Fig. 1a) together with the spectra of α-Fe_2O_3 etalon (Fig. 1c) and α-FeOOH used in hydrothermal synthesis (Fig. 1b). The Mössbauer spectra of the hydrothermal products obtained by heating the autoclave up to 260, 280 and 300° C are presented in Fig. 2. At 260° C, the Mössbauer spectrum belongs to the α-FeOOH phase. Thermal treatment up to 280° C leads to the appearance of the α-Fe_2O_3 phase in the Mössbauer spectrum. The spectrum of the sample obtained at 300° C is a superposition of α-Fe_2O_3 and $BaFe_{12}O_{19}$ phases. At these temperatures the experiments were done for different times of thermal treatment (up to 24 h). The X-ray spectra show the formation of a $BaFe_{12}O_{19}$ lattice for 20 h at 280° C and ~10 h at 300° C (Figs. 3 and 4). For a thermal treatment of 24 h at 260° C, the only iron

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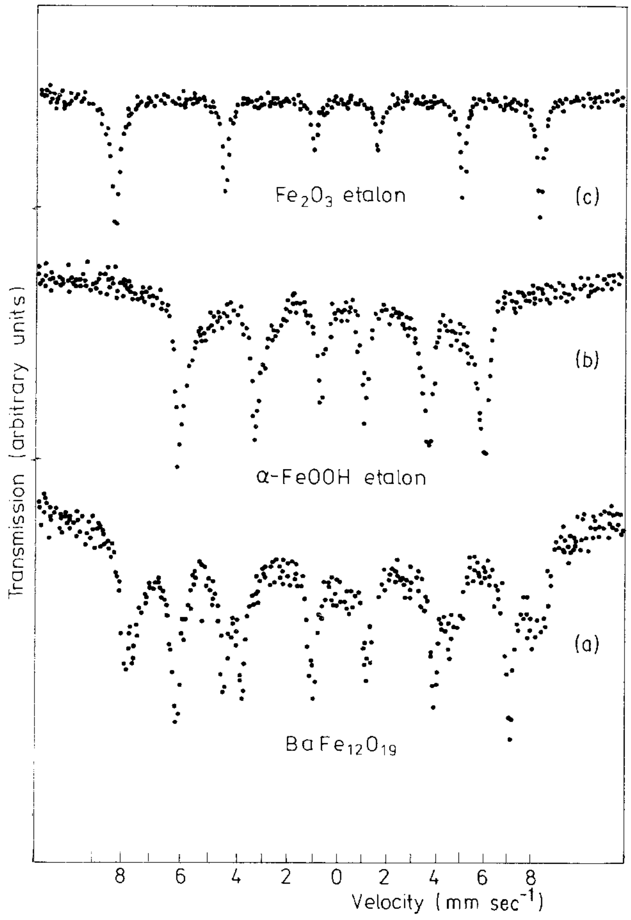

Figure 1 Mössbauer spectra of (a) $BaFe_{12}O_{19}$, (b) α-FeOOH, (c) α-Fe_2O_3 etalon.

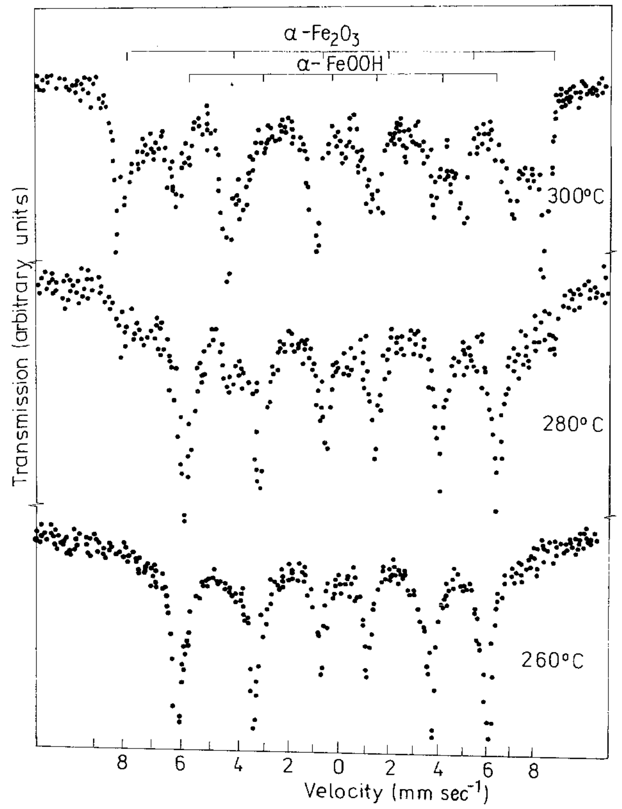

Figure 2 Mössbauer spectra of hydrothermal products obtained by heating the autoclave up to 260, 280 and 300° C.

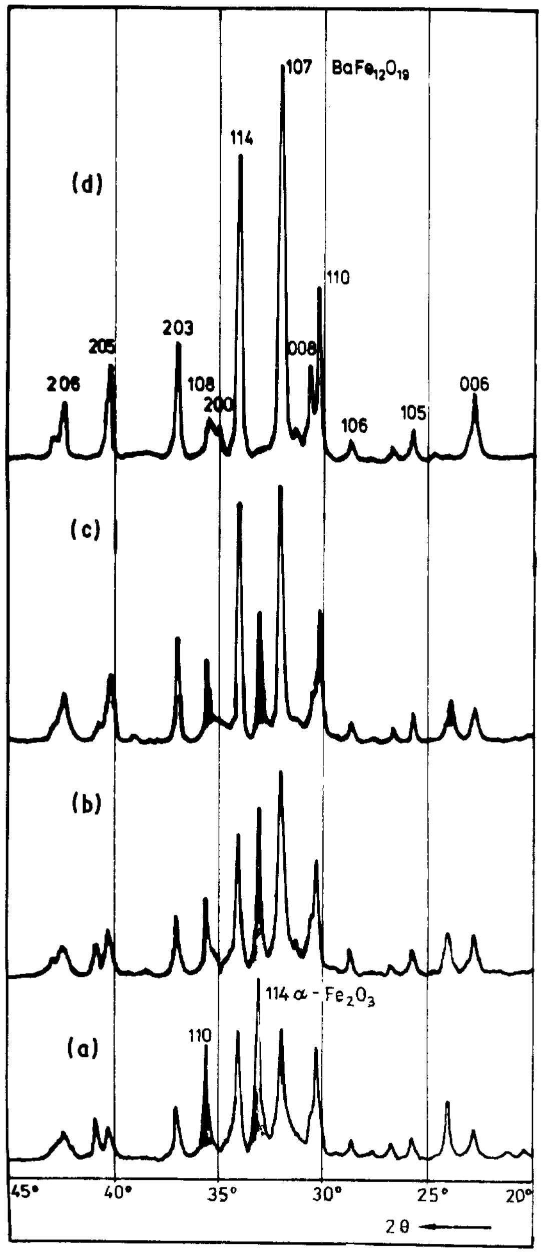

Figure 3 X-ray diffraction patterns of hydrothermal products obtained at 280° C, for different thermal treatment times: (a) 1 h, (b) 4 h, (c) 10 h, (d) 20 h.

phase identified in the reaction product was α-Fe_2O_3.

The temperature dependence of the saturation magnetization and residual induction of the hydrothermal products is shown in Fig. 5. There is no significant change of these parameters in the temperature range 300 to 325° C; one can choose for optimum a temperature of 315 ± 5° C. The corresponding vapour pressure is of the order of 98 to 110 atm. The optimum concentration of reactants (wt %) was: 14.8% $Ba(OH)_2 \cdot 8H_2O$, 33.5% α-FeOOH, 51.7% H_2O. The fill factor was taken to be about 0.54

The X-ray data for the sample obtained at 300° C for 20 h of thermal treatment confirm the structure of $BaFe_{12}O_{19}$ (Table I). By fitting the Mössbauer spectrum of this sample, the characteristic five iron sublattices of barium hexaferrite are shown (Fig. 6). The general morphology of hydrothermally obtained barium hexaferrite is given by the hexagonal crystals ($\sim 1\ \mu$m in width and $\sim 0.1\ \mu$m thickness) with quite a perfect lattice as indicated by electron diffraction and

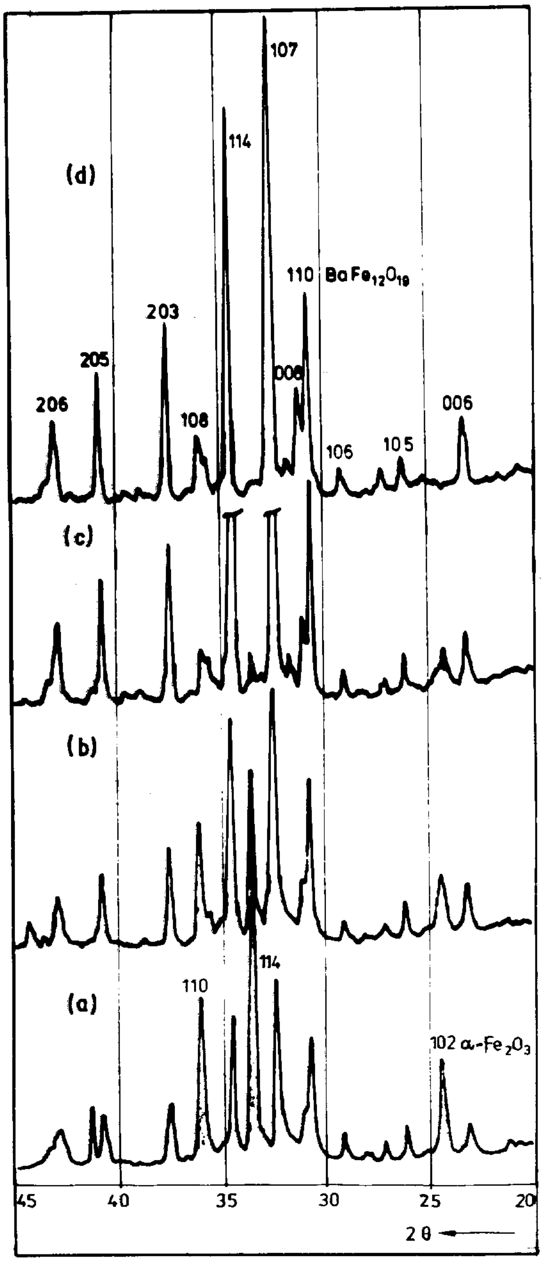

Figure 4 X-ray diffraction patterns of hydrothermal products obtained at 300° C, for different thermal treatment times: (a) 1 h, (b) 4 h, (c) 10 h, (d) 20 h.

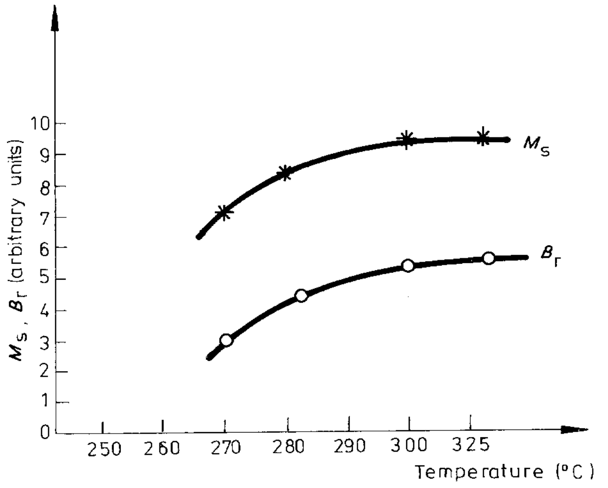

Figure 5 The saturation magnetization and residual induction as a function of reaction temperature (reaction time ~ 20 h).

TABLE I X-ray powder diffraction data for hydrothermally synthesized $BaFe_{12}O_{19}$

hkl	ASTM 7–276		Observed values	
	d_{hkl} (nm)	I/I_0	d_{hkl} (nm)	I/I_0
101	0.494	10	0.495 ± 0.002	6
102	0.465	13	0.465 ± 0.002	10
006	0.386	15	0.385 ± 0.002	15
105	–	–	0.343 ± 0.002	8
106	–	–	0.309 ± 0.002	7
110	0.294	40	0.2935 ± 0.002	43
008	0.289	13	0.289 ± 0.001	15
112	0.285	10	0.284 ± 0.001	6
107	0.277	100	0.277 ± 0.001	100
114	0.262	100	0.262 ± 0.001	81
200	0.255	8	0.2545 ± 0.0006	10
108	0.252	8	0.2516 ± 0.0006	13
203	0.242	40	0.2418 ± 0.0006	38
205	0.223	40	0.2233 ± 0.0006	30
206	0.213	25	0.2123 ± 0.0006	20
10.11	0.1945	10	0.1947 ± 0.0005	6
11.10	0.1814	15	0.1811 ± 0.0005	8
210	0.1715	5	0.1716 ± 0.0005	3
126	0.1699	10	0.1698 ± 0.0004	7
127	0.1666	40	0.1664 ± 0.0004	27
304	0.1625	50	0.1624 ± 0.0004	38

electron microscopy investigations (Fig. 7). The most probable growing mechanism of barium hexaferrite in hydrothermal conditions is at the emergency steps of helicoidal dislocations [16].

The magnetic characteristics of the isotropic magnets obtained were determined by means of the Walker hysteresisgraph. The hysteresis loops were obtained with an accuracy within ±2.0%. The following magnetic parameters characterize the magnets: coercive force $H_c \sim 159\,\text{kA}\,\text{m}^{-1}$, residual induction $B_r \sim 0.26\,\text{T}$, maximum energy product $(BH)_{\max} \sim 12\,\text{kJ}\,\text{m}^{-3}$ at a density of about $4.8\,\text{g}\,\text{cm}^{-3}$. It is well known that in the conventional procedure the formation of barium hexaferrite is always preceded by the intermediate phase $BaFe_2O_4$ [17]. Our Mössbauer, X-ray, electron microscopy and electron diffraction investigations have demonstrated the appearance of α-Fe_2O_3-like intermediate phase in hydrothermal syntheses of barium hexaferrite. A similar behaviour was observed in chemically coprecipitated barium hexaferrite where $BaFe_2O_4$ (and α-Fe_2O_3) was not identified in the reaction process [8].

The main differences between the hydrothermal procedure and the conventional one are presented in Fig. 8. It can be observed that the temperature required by the hydrothermal procedure is lower (~ 315° C) than the temperature for firing in the conventional process (1150 to 1250° C). In addition a few intermediate steps of the conventional procedure (granulation, grinding) are not necessary in the hydrothermal method.

4. Conclusions

The hydrothermal method was found to be suitable for the synthesis of stoichiometric barium hexaferrite from an aqueous solution of $Ba(OH)_2 \cdot 8H_2O$ and α-FeOOH. The appearance of $BaFe_{12}O_{19}$ in the hydrothermal process is preceded by the formation of an α-Fe_2O_3 phase. The following reaction conditions

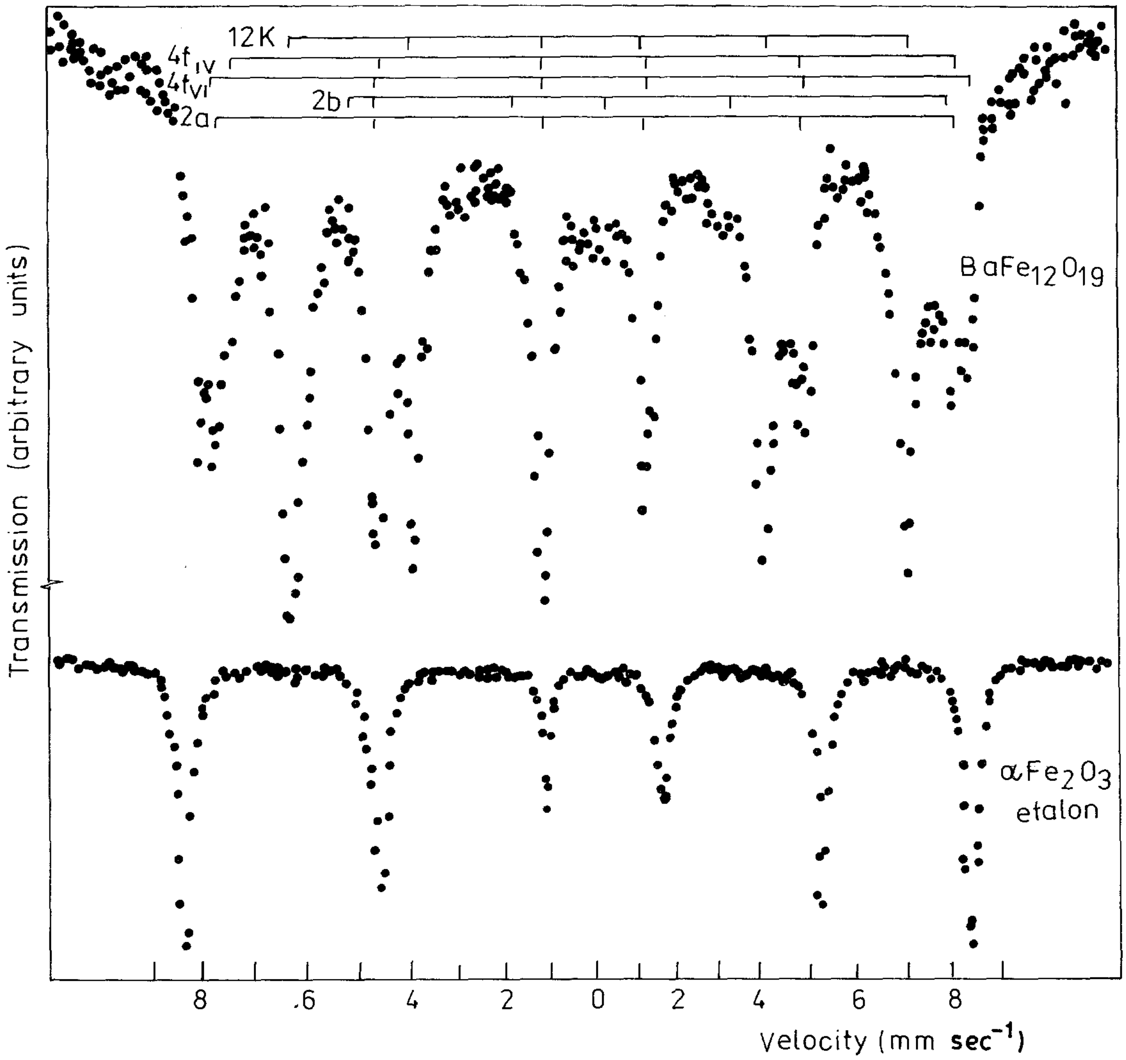

Figure 6 Five sublattice Mössbauer spectrum of hydrothermally synthesized $BaFe_{12}O_{19}$.

are required:

(i) concentration of reactants (wt %): 14.8 % $Ba(OH)_2 \cdot 8H_2O$, 33.5 % α-FeOOH, 51.7 % H_2O;

(ii) temperature 315 ± 5° C;

(iii) heating rate 2 to 3° C min^{-1};

(iv) vapour pressure 98 to 110 atm;

(v) thermal treatment time ~20 h;

(vi) filling factor ~0.54.

Taking into account the values of the magnetic parameters obtained for isotropic magnets it seems that hydrothermal synthesis is a suitable procedure to obtain barium hexaferrite magnets.

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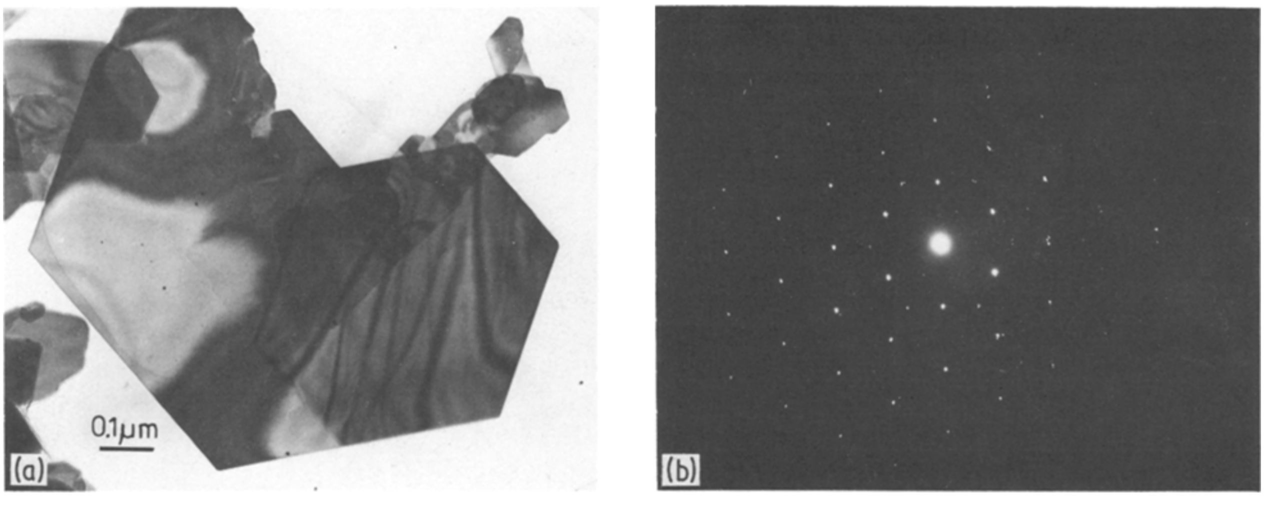

Figure 7 (a) Transmission electron microscopy and (b) electron diffraction images of hydrothermally obtained $BaFe_{12}O_{19}$.

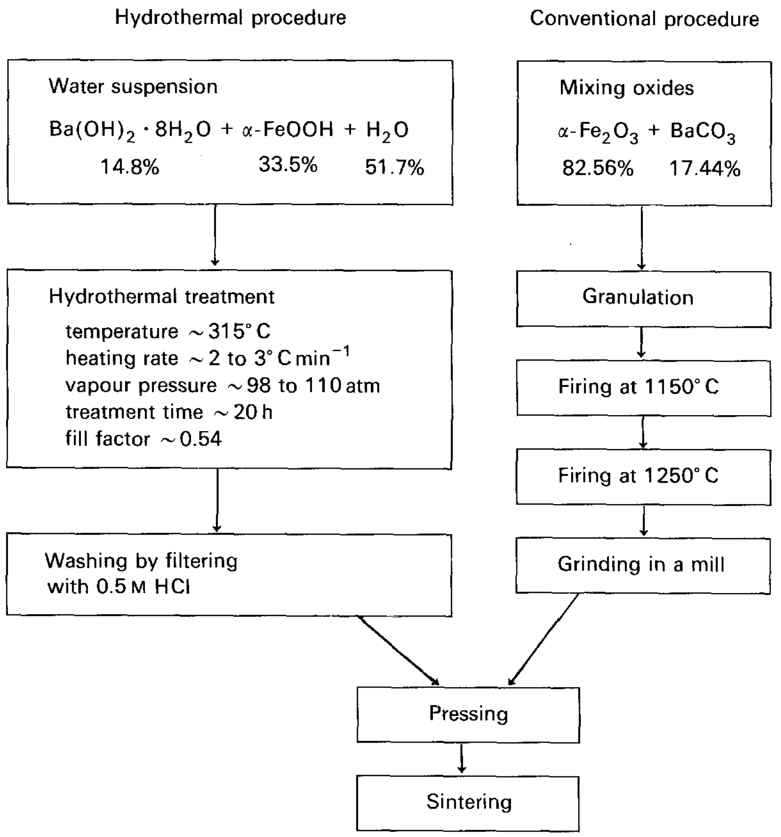

Figure 8 Comparison between hydrothermal and conventional procedures for preparing barium hexaferrite.

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