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Synthesis of ultrafine particles of barium ferrite by chemical coprecipitation

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A new method to synthesize barium hexaferrite by chemical coprecipitation is described. A mixed precursor was precipitated by addition of a barium salt to a strongly alkaline ferrate (VI) solution. The precursor yielded barium hexaferrite on heating for 6 h at 800 °C; partial transformation was evident even at lower temperatures, from X-ray patterns and Mössbauer spectra. Scanning electron microscopy of the powders fired at 800 °C, showed that the particles were less than 0.5 μm in diameter.

1. Introduction

Barium hexaferrite, $BaO \cdot 6\ Fe_2O_3$ is an important hard magnetic material because of its large coercive force, which is derived from the large magnetocrystalline anisotropy. The traditional synthesis procedure involves the solid-state reaction of barium carbonate and haematite.

The theoretical intrinsic coercivity can only be approached when the particle size is below 1 μm, and the high temperature used (1200 °C) provides conditions for crystal growth well above this value. Therefore, extensive grinding is required to decrease crystal size, and grinding gives rise to lattice strains that unfavourably affect magnetic properties. Furthermore, the solid-state reaction proceeds through the formation of several intermediate phases. Okazaki *et al.* [1], described the formation of three compounds $2BaO \cdot Fe_2O_3$, $BaO \cdot Fe_2O_3$ and $BaO \cdot 6Fe_2O_3$ in the temperature range 1000–1380 °C. Below 1000 °C, the formation of $BaO \cdot Fe_2O_3$, $BaO \cdot 2Fe_2O_3$ and $BaO \cdot 6Fe_2O_3$, was described by Erchak *et al.* [2] and by Goto and Takada [3].

Alternatively, wet synthesis procedures have been developed. Usually, these procedures involve the coprecipitation of ferrihydrite, or amorphous ferric hydrous oxide, and barium hydroxide, followed by calcination to relatively low temperatures. Thus, Haneda *et al.* [4], coprecipitated iron and barium by pouring an aqueous solution of ferric and barium chlorides, into a solution of sodium hydroxide and sodium carbonate. The resulting precipitate was washed and dried at temperatures between 700 and 1100 °C. $BaFe_{12}O_{19}$ was formed at a relatively low temperature and heating at 925 °C led to a highly coercive barium ferrite [5, 6].

In this paper we describe an alternative synthesis procedure that involves coprecipitation of a precursor from a strongly alkaline solution in the presence of an oxidant, such as sodium hypochlorite, to generate ferrate(VI) species [7].

2. Experimental procedure

2.1. Synthesis of the precursor

Gaseous chlorine was bubbled through a concentrated (10 M) solution of sodium hydroxide (NaOH), to generate an approximately 3 M solution of sodium hypochlorite (NaClO), also 3 M in sodium chloride (NaCl). The solution was filtered through fritted glass under cooling to minimize silicate attack, and $Fe(NO_3)_3 \cdot 9H_2O$ was added to yield a 0.55 M iron solution.

The deep purple ferrate solution was filtered again and $BaCl_2 \cdot 2H_2O$ was added to reach the desired Ba:Fe ratio. The mixture evolved rapidly into a slurry, with strong oxygen evolution.

The slurry was left standing for 24 h, further treated at 80 °C for 1 h, and left in storage at room temperature.

Aliquots were filtered through fritted glass, rinsed several times with $H_2O:C_2H_5OH$ (50:50) to remove residual chloride, and $(C_2H_5)_2O$ to remove alcohol. The solid was left overnight in an oven at 110 °C.

2.2. Thermal treatment and characterization of the solid

Samples were heated up to 710 and 800 °C and maintained at these temperatures for 6 h, in an electric furnace in an air atmosphere. Cooling was performed at a slow cooling rate.

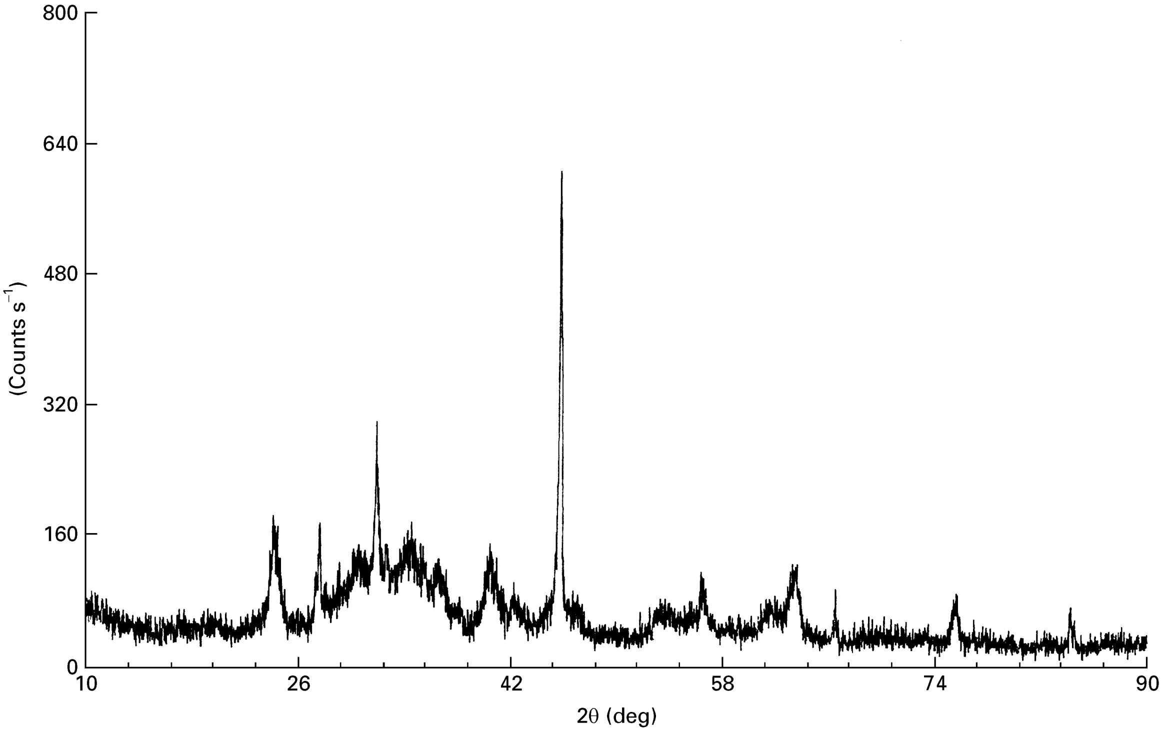

Figure 1 X-ray diffraction pattern of the precursors heated at 110 °C overnight.

The solids were characterized by X-ray Diffraction (XRD), scanning electron microscopy (SEM) and Mössbauer spectroscopy. The instruments used for characterization were a Rigaku 0–20 X-ray powder diffractometer ($CuK_{\alpha}\lambda = 0.54$ nm), a Philips SEM model 515 and a conventional ^{57}Fe Mössbauer transmission equipment (ELSCENT), using the constant acceleration method.

Chemical analyses were also routinely carried out, both on the solids and supernatant liquids. Iron and barium were determined by atomic absorption spectrometry.

All reagents were analytical grade.

3. Results

Barium ferrate(VI) is well known [7], and the precipitation of relative pure (86.7%) barium ferrate(VI) from aqueous solution has been described [8]. The experimental conditions used in this study do not, however, lead to the precipitation of $BaFeO_4$: the Ba/Fe ratios explored were too low, and the chemical composition of the solid reflected these ratios (see below).

The precursor obtained in this work was a mixture of crystalline $Ba(OH)_2{\cdot}2H_2O$ and amorphous Fe_2O_3. Fig. 1 shows a diffractogram of the solid obtained after drying overnight at 110 °C. Weak and broad lines are observed, suggesting the presence of the crystalline form of $Ba(OH)_2{\cdot}2H_2O$ and eventually NaCl. EDS shows that, within the sampling volume of the technique (1 μm^3), the composition was homogeneous and constant. Neither chlorine nor sodium were detected in adequately washed samples.

The mixture obtained was an excellent precursor for $BaO{\cdot}6Fe_2O_3$. Fig. 2 shows that, after 6 h treatment at 710 °C, the most intense diffraction peaks were already due to the hexagonal ferrite, although unreacted barium oxide was still present.

Further treatment at 800 °C for 6 h produces highly crystalline pure barium hexaferrite, as shown in Fig. 3.

The ratio Ba:Fe in the starting solution was crucial in determining the purity. Best results were achieved by using a slight barium excess, because barium hydroxide is rather soluble in water. The best ratio was 1.2:12 rather than 1.0:12. When this ratio was used, the excess barium remained in the residual solution.

BaO from unreacted $Ba(OH)_2{\cdot}2H_2O$ was still detected in the solid sintered at 710 °C (Fig. 2), but it disappears upon further heating at higher temperatures (Fig. 3). Fig. 4a and b present, respectively, SEM images of precursor samples obtained after overnight drying at 110 °C, and of the solid obtained by heating at 800 °C for 6 h. The evolution of the $Ba(OH)_2$ platelets to barium hexaferrite single-crystal particles is apparent. The size of the latter particles is variable, with some large (a few micrometres) and many smaller particles (in the range 0.1–0.5 μm); the good crystallinity and particle-size range are adequate for good magnetic properties.

The Mössbauer spectrum of the sample calcined at 800 °C shows the typical pattern of four sextuplets due to the ($2a + 4f_1$), 12k, $4f_2$ and 2b iron ions (see Fig. 5). The resolution of the peaks and the hf parameters (shown in Table I) demonstrate the formation of the well-crystallized barium hexaferrite [9–11].

4. Discussion

It is possible to find reports in the literature on the synthesis of barium hexaferrite by oxidative precipitation of ferric oxides from ferrous salts [12], in the presence of barium salts. However, the precipitation

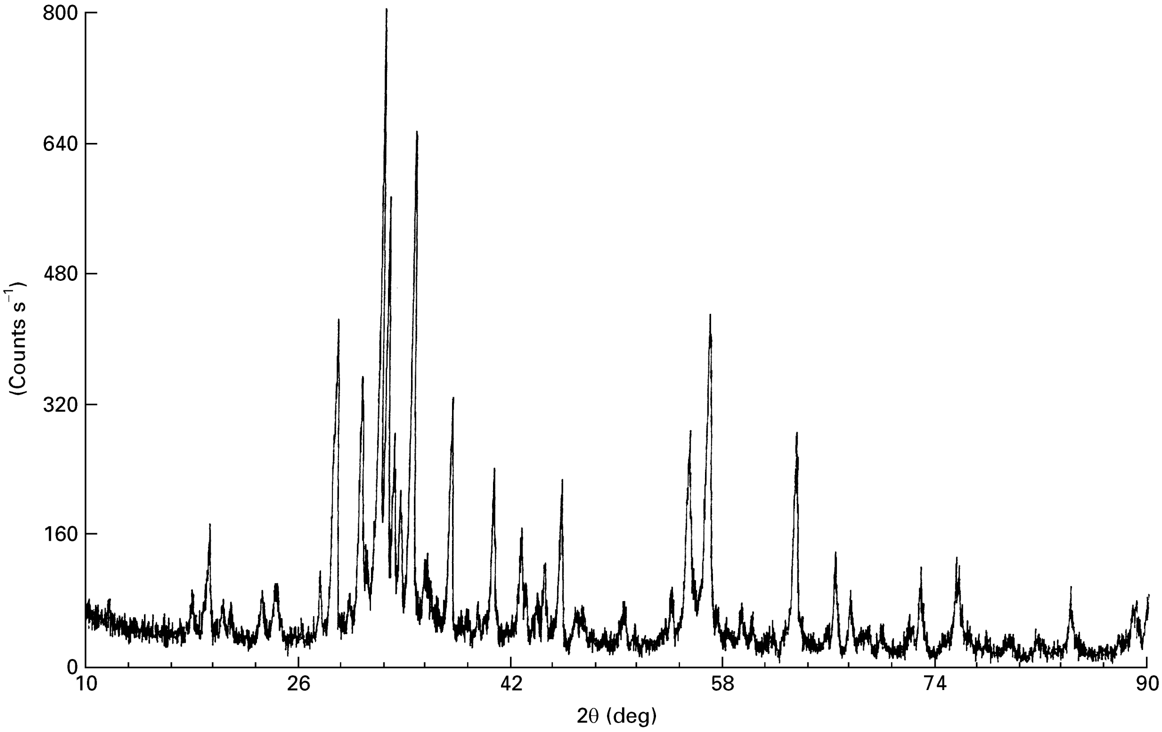

Figure 2 X-ray diffraction pattern of the precursors heated at 710 °C for 6 h.

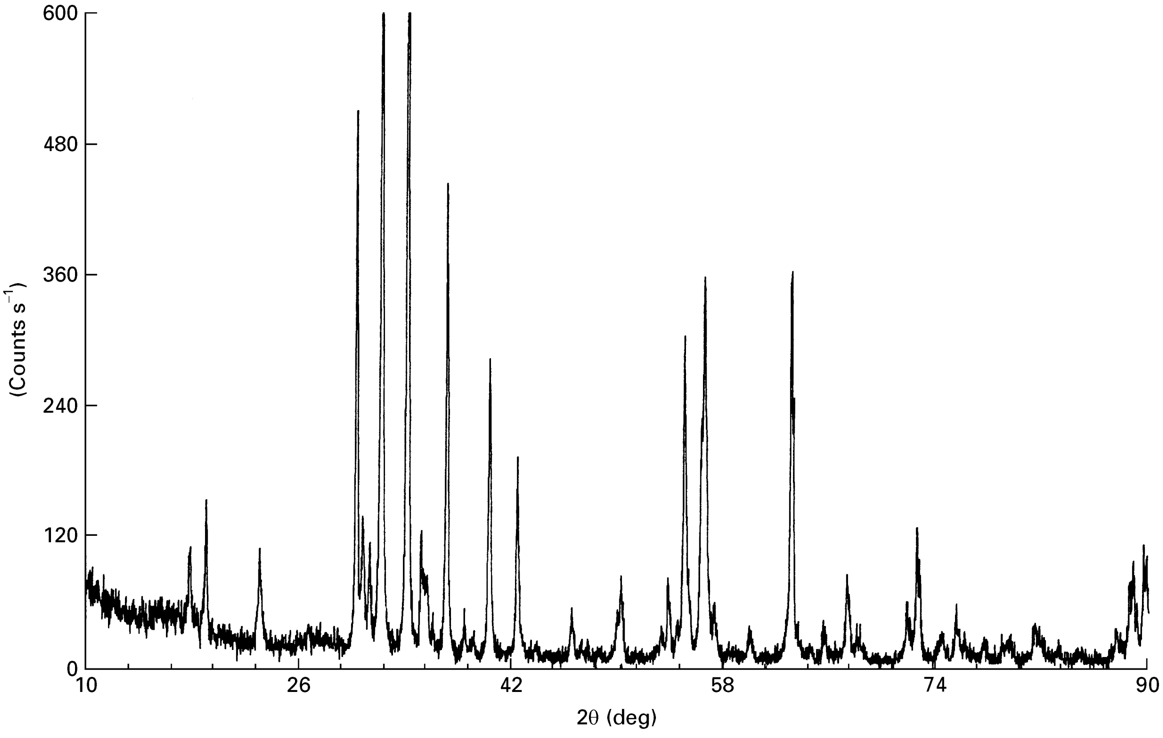

Figure 3 X-ray diffraction pattern of the precursors heated at 800 °C for 6 h.

mechanism of oxidative iron oxides is not adequate for this purpose, since this way of synthesis was not confirmed by later work [12]. In this process, the precursor is ferrous hydroxide formed as hexagonal platelets [12]; the space group is D5. This compound directs the oxidation in alkaline media to spinel-type structures, the surface of the platelets acting as sites for heterogeneous nucleation of the new phase.

In the procedure described here, the only crystalline material in the precursor is Ba(OH)$_2$·nH$_2$O, and the structural evolution is strongly influenced by this material. The amorphous iron oxide obtained under our conditions is ferrihydrite, which is known to be structurally related to the hexagonal iron oxides such as aFe$_2$O$_3$. Again, the structural similarity with barium hexaferrite favours the evolution of this phase during thermal treatment. Although there is no actual information about the changes taking place during this transformation, it may be visualized that the precursor provides pre-assembled Fe$_2$O$_3$ and BaO layers of the type present in barium hexaferrite.

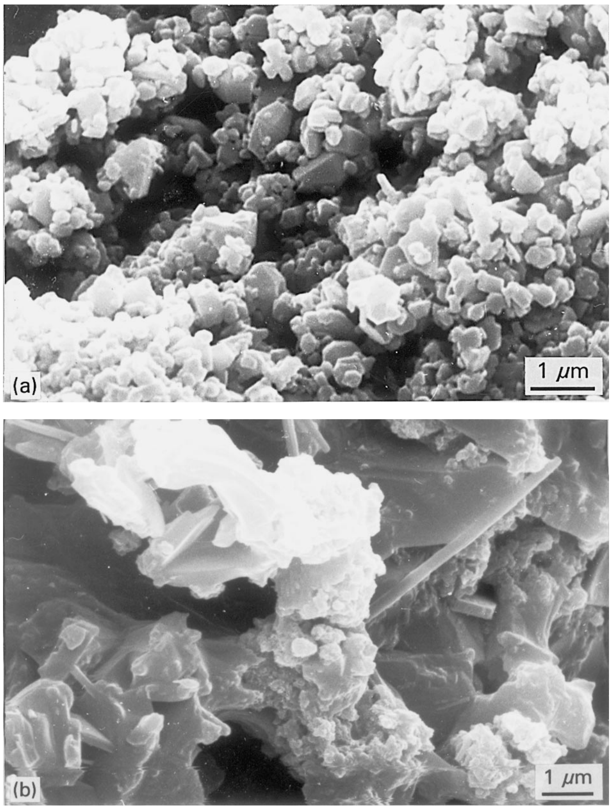

Figure 4 Scanning electron micrographs of (a) precursors particles obtained by heating at 110 °C overnight, and (b) hexaferrite particles obtained by heating at 800 °C for 6 h.

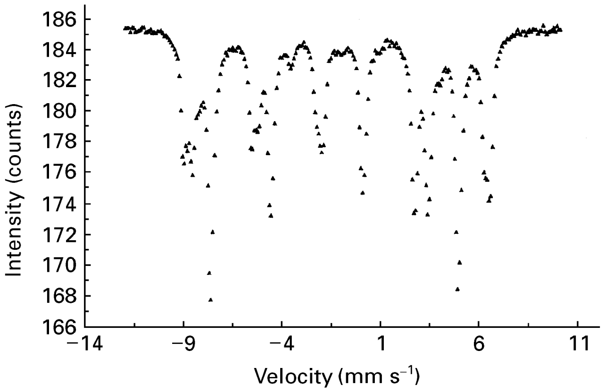

Figure 5 Mössbauer spectrum of the sample obtained by heating at 800 °C for 6 h.

The process described here shares most of the advantages of the previously described wet synthesis procedures [4]: intimate mixture of the constituents in the precursor and good magnetic properties of the crystalline material. The enhancement of the solubility of iron in alkaline media by oxidation to the + VI state permits precipitation of the precursor by mixing solutions of both ions. A potential problem of inhomogeneity may be encountered when the precursor is synthesized by pouring Fe^{3+} and Ba^{2+} salts into a strongly alkaline medium, because of the very different solubilities of both ions in the medium. This problem is less important in our procedure; although a more ellaborate previous synthesis procedure is required, the chemicals involved are cheap and the process itself is not complex.

Ross [5] has shown that precursors obtained by wet methods do not produce mixed oxides other than the hexaferrite upon heating. In our synthesis, the hexaferrite is not the only detected phase; it is well formed at temperatures at $T < 800$ °C, well below the temperature of 925 °C used by Ross. Furthermore, the hexaferrite is already formed at 710 °C, even though some unreacted barium oxide remains (see Fig. 2). There is also some evidence of mixed oxide formation at much lower temperatures.

TABLE I Mössbauer parameters of barium ferrite

hf parameters	Crystallographic site			
	12k	$4f_2$	$4f_1$ + 2a	2b
Isomer shift, (+ 0.02 mm s^{-1}) w.r.t. metallic iron	0.36	0.37	0.25	0.28
Quadropole splitting, E (+ 0.02 mm s^{-1})	0.44	0.14	0.24	2.25
Hyperfine field, H_n (+ 0.5T)	42.8	52.8	50.6	41.5

These results are to be contrasted with the thermal evolution of the precursor obtained from Fe(III) solutions. According to Ross [5], up to 740 °C, the main changes are associated with H_2O (and other possible volatiles) loss, and only at these temperatures does the hexaferrite begin to form. The evolution of the precursor will be the subject of a separate detailed thermogravimetric and Mössbauer study.

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