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The Thermal Evolution of a Barium Ferrite Precursor Obtained by a New Chemical Coprecipitation Method

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Abstract: The evolution during thermal treatment of the precursor obtained by a new method to synthesize barium hexaferrite by chemical coprecipitation is described; the method involves the precipitation from a strongly alkaline ferrate(VI) solution containing barium chloride. Barium hexaferrite may be formed by heating of the original superparamagnetic precursor at temperatures as low as 700°C as shown by XRD, Mössbauer spectra and DTA-TGA behaviour. The precursor does not contain appreciable amounts of carbonate, thus favouring the formation of the hexaferrite at lower temperatures. Scanning electron microscopy shows that the ferrite particles are less than 0.5 µm in diameter.

1. INTRODUCTION

The traditional synthetic procedure for barium hexaferrite, $\text{BaO} \cdot 6 \text{Fe}_2\text{O}_3$, involves the solid state reaction of barium carbonate and hematite at 1200°C. The reaction proceeds through the formation of several intermediate phases, such as $2\text{BaO} \cdot \text{Fe}_2\text{O}_3$, $\text{BaO} \cdot \text{Fe}_2\text{O}_3$ and $\text{BaO} \cdot 2\text{Fe}_2\text{O}_3$, and $\text{BaO} \cdot 6\text{Fe}_2\text{O}_3$ [1-3]. Other problems are the large crystal size and crystal strains, that lowers the coercivity. Wet synthetic procedures usually involve the coprecipitation of ferrihydrite, or amorphous ferric hydrous oxide, and barium hydroxide, followed by calcination to relatively low temperatures. Under these conditions, $\text{BaFe}_{12}\text{O}_{19}$ is formed at a relatively low temperatures and heating at 925°C leads to a highly coercive barium ferrite [4-5]. In this paper we describe the characteristics of barium hexaferrite synthesized by a procedure described by us [6], that involves coprecipitation of a precursor from a strongly alkaline solution in the presence of an oxidant (sodium hypochlorite) to generate ferrate(VI) species.

2. EXPERIMENTAL

2.1 Synthesis of the precursor

The procedure was described earlier [6]. $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ was added to an approximately 3 M solution of sodium hypochlorite (also 3 M in NaCl) to yield a 0.55 M iron solution. $\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$ was added to the filtered deep purple ferrate solution in adequate amounts 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 one hour, and left in storage at room temperature. Aliquots were filtered through fritted glass, rinsed several times with $\text{H}_2\text{O}:\text{C}_2\text{H}_5\text{OH}$ (50:50) to remove residual chloride, and $(\text{C}_2\text{H}_5)_2\text{O}$ to remove alcohol. The solid was left overnight in an oven at 110°C.

2.2 Thermal treatment and characterization of the solid.

The evolution of the solid upon thermal treatment was followed by thermogravimetry, differential thermal analysis, X-Ray Diffraction (XRD), scanning electron microscopy (SEM), Fourier Transform Infrared Spectroscopy, and Mössbauer spectroscopy. The instruments used for characterization were a Mettler TA 3000 Thermoanalyzer, a RIGAKU 0-20 X-Ray Powder Diffractometer ($\text{CuK}\alpha = 1.54\text{\AA}$),

a PHILIPS SEM model 515 with an EDS probe, a Nicolet FTIR apparatus, and a conventional ^{57}Fe Mössbauer transmission equipment (ELSCINT), using the constant acceleration method. Fe and Ba were determined by atomic absorption spectrometry. All reagents were analytical grade.

3. RESULTS

The X-ray diffractogram of the solid obtained after overnight drying at 110°C suggests the presence of crystalline $\text{Ba}(\text{OH})_2 \cdot 2\text{H}_2\text{O}$. EDS shows that, within the sampling volume of the technique ($\sim 1\mu\text{m}^3$), the composition is homogeneous and constant; washing removes all NaCl seen in the original samples. The mixture obtained is an excellent precursor for $\text{BaO} \cdot 6\text{Fe}_2\text{O}_3$. After six hours treatment at 710°C , the most intense diffraction peaks are already due to the hexagonal ferrite, although unreacted barium oxide is still present. Figure 1 shows that heating at 800°C for six hours produces highly crystalline pure barium hexaferrite. The stoichiometric solid is best obtained when a slight barium excess is used in the original solution; the excess barium remains dissolved. BaO from unreacted $\text{Ba}(\text{OH})_2 \cdot 2\text{H}_2\text{O}$ is still detected in the solid sintered at 710°C , but it disappears upon further heating at higher temperatures. SEM examination of the precursor, and of the solid obtained by heating at 800°C for six hours show the evolution of the $\text{Ba}(\text{OH})_2$ platelets to barium hexaferrite single crystal particles; the good crystallinity and particle size range are adequate for good magnetic properties. Fig. 2 shows the hysteresis curve. The Mossbauer spectra of samples calcined at different temperatures, in the range 110 – 800°C show the evolution from a superparamagnetic material to the typical hexaferrite pattern of four sextuplets due to the $(2a+4f_1)$, $12k$, $4f_2$ and $2b$ iron ions. The resolution of the peaks and the hf parameters demonstrate that already at 700°C , well crystallized barium hexaferrite forms. FTIR spectra of the precursors and of a thermally treated sample demonstrates that carbonate contents is very low, as expected if due precautions are taken to protect the solutions from contact with air.

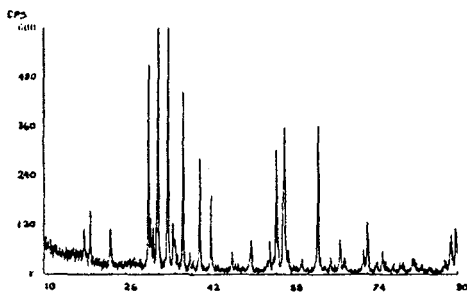


Figure 1: XR diffractogram of the synthesized hexaferrite

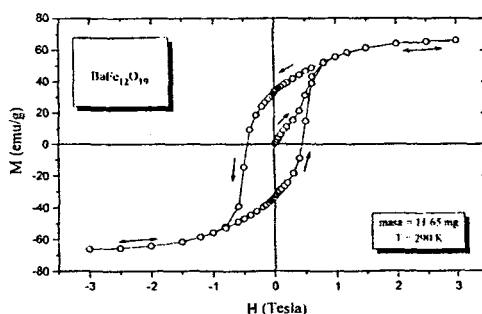


Figure 2: Hysteresis curve

4. DISCUSSION

The amorphous iron oxide obtained in our conditions is ferrihydrite, which is known to be structurally related to the hexagonal iron oxides such as $\alpha\text{Fe}_2\text{O}_3$. The structural similarity with Ba-hexaferrite, and the intimate mixture with barium hydroxide platelets, makes easy the evolution to the ferrite. The use of a strongly oxidant alkaline solution, largely enhances iron solubility, and permits to precipitate simultaneously both ions. The hexaferrite is the only detected mixed oxide in the thermally treated samples, and the Mossbauer spectra demonstrate that 700°C suffices to produce it, well below the temperature of 925°C used by Ross [5]. The evolution from superparamagnetism to ferrimagnetism takes place at surprisingly low temperatures; a detailed study of the site occupancies as a function of temperature is underway. DTA studies shows that the exothermic peak, characteristic of hexaferrite crystallization is centered at 730°C , when the heating rate is 6 K min^{-1} (sample mass, ca. 50 mg). The absence of carbonate is probably responsible for the high reactivity of barium.

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