



Structural properties of ultrafine Ba-hexaferrite nanoparticles

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ABSTRACT

Crystal structure of ultrafine Ba-hexaferrite ($\text{BaFe}_{12}\text{O}_{19}$) nanoparticles was studied using X-ray diffractometry (XRD), high-resolution transmission electron microscopy (HRTEM), energy-dispersive X-ray spectroscopy (EDXS), X-ray absorption fine structure (XAFS), and Mössbauer spectroscopy (MS), to be compared to the structure of larger nanoparticles and the bulk. The nanoparticles were synthesized with hydrothermal treatment of an appropriate suspension of Ba and Fe hydroxides in the presence of a large excess of OH^- . The ultrafine nanoparticles were formed in a discoid shape, ~ 10 nm wide and only ~ 3 nm thick, comparable to the size of the hexagonal unit cell in the c -direction. The HRTEM image analysis confirmed the hexaferrite structure, whereas EDXS showed the composition matching the $\text{BaFe}_{12}\text{O}_{19}$ formula. XAFS and MS analyses showed considerable disorder of the structure, most probably responsible for the low magnetization.

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1. Introduction

Due to the small size and a large proportion of all atoms located at the surface or close to it, the nanoparticles exhibit a structure different from the corresponding bulk. This adaptation of the crystal structure of the nanoparticles to the small size was intensively studied in some materials with a relatively simple structure, for example in cubic spinel ferrites [1–3], whereas for the nanoparticles with more complex structure and/or composition the data remain scarce. The reason for that, at least to some extent, lies in the difficulty of synthesizing ultrafine nanoparticles of complex compounds. While the synthesis of small nanoparticles of simple semiconductors, metals and oxides is generally relatively simple, the synthesis of more complex compounds and alloys with a large unit cell remains a challenge.

One of magnetic materials that cannot be easily synthesized in the form of ultrafine nanoparticles is barium M hexaferrite ($\text{BaFe}_{12}\text{O}_{19}$). Barium hexaferrite crystallizes in a hexagonal structure ($a=0.587$ nm, $c=2.31$ nm), which can be represented as a stacking of close-packed layers composed of larger oxygen and barium ions with smaller iron ions at the interstitial positions. The structure can be divided into alternating structural blocks: the S block ($(\text{Fe}_6^3+\text{O}_8^2-)^{2+}$) composed of the two layers containing only oxygen ions, and the R block ($(\text{BaFe}_6^3+\text{O}_{11}^2-)^{2-}$) composed

of the three layers in a hexagonal stacking, where the middle layer also contains barium ions [4,5]. To form hexaferrite, high temperatures above 600 °C are usually needed, which makes the synthesis of the ultrafine nanoparticles very difficult [4].

Recently, we reported the synthesis of ultrafine particles of Ba hexaferrite using a modified hydrothermal method [6,7]. For the synthesis, the Ba and Fe hydroxides were hydrothermally treated in the presence of high excess of hydroxyl ions. The formation temperature of hexaferrite decreases with increasing excess of hydroxide, in extreme case below 100 °C [8]. At the temperatures just above the formation temperature, ultrafine nanoparticles were obtained. In the range of 10 – 30 °C above the formation temperature, larger platelet particles appeared through the secondary re-crystallization (Ostwald ripening) [6]. The start temperature of the secondary re-crystallization can be highly increased by addition of oleic acid as surfactant. The addition of oleic acid enabled synthesis of the ultrafine nanoparticles in a broad temperature range up to 270 °C, but their size remained almost unchanged [6].

The ultrafine nanoparticles had a discoid shape, around 10 nm wide, but only approximately 3 nm thick [6–8]. Remarkably, in the direction of the c -axis of the hexagonal structure, the particles were less than two unit cells thick. According to the composition, which matched the nominal $\text{BaFe}_{12}\text{O}_{19}$ formula within the error margin of the energy-dispersive X-ray spectroscopy (EDXS) of a transmission electron microscope (TEM) [7], the nanoparticles could be considered as barium ferrite. The structure of the ultrafine nanoparticles, on the other hand, could not be easily

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determined. Due to the small thickness of the discoid nanoparticles, X-ray diffractometry (XRD) provided little information on the structure in the *c*-direction, characteristic for hexaferrite. High-resolution electron microscopy (HREM) imaging showed a period of 1.15 nm matching the periodicity of the (0 0 2) planes of the hexaferrite structure [8]. Magnetic measurements, however, showed a lack of magnetic structure typical of hexaferrite. The ultrafine nanoparticles exhibited weak ferrimagnetism with a magnetization below 2 Am²/kg at 1 T, much lower than the saturation magnetization 72 Am²/kg of the bulk Ba-hexaferrite [6–8].

In the present study, the structure of the hydrothermally-synthesized ultrafine Ba-hexaferrite nanoparticles has been investigated with a combination of XRD, HREM, X-ray absorption fine structure (XAFS) and Mossbauer spectroscopy (MS), and compared to the structure of larger particles and the bulk.

2. Experimental

2.1. Synthesis of nanoparticles

The Ba-hexaferrite nanoparticles were synthesized using hydrothermal method described by Primc et al. [6]. The size and morphology of the nanoparticles was controlled by varying the temperature and using the addition of oleic acid. In brief, 400 mL of the aqueous solution of iron and barium nitrates ($c(\text{Fe}^{3+}) = 0.05 \text{ mol/L}$, $c(\text{Ba}^{2+}) = 0.01 \text{ mol/L}$, $\text{Fe}^{3+}/\text{Ba}^{2+} = 5$) was mixed with

NaOH (2.72 mol/L), to reach a $[\text{OH}^-]/[\text{NO}_3^-]$ ratio equal to 16. The mixture was then sealed in a 1000-mL Inconel autoclave vessel (Model 4522 M, Parr Instrument Co) and heated at a rate of 3 °C/min to a target temperature between 150 and 270 °C. Several target temperatures in the range were chosen. When the autoclave reached the temperature it was turned off. The temperature inside the autoclave started to decrease after approximately 10 min. Upon cooling off the product nanoparticles were thoroughly washed with a diluted aqueous solution of acetic acid (10%) to dissolve any Ba-rich compounds formed as a consequence of the barium excess. Finally, the nanoparticles were washed with distilled water, and dried at 60 °C in ambient air. Table 1 lists the experimental conditions in the synthesis of the different samples.

With hydrothermal treatment at a low temperature of 150 °C, the vast majority of synthesized Ba hexaferrite was in the form of uniform, ultrafine, discoid nanoparticles, ~10 nm wide and ~3 nm thick (Fig. 1(a)). A few individual larger platelet crystallites (marked with arrow) were occasionally present as a consequence of the secondary re-crystallization, i.e., Ostwald ripening. In the Ostwald ripening process, a few large particles undergo exaggerated growth at the expense of the smaller ones. Even a small number of these larger crystallites can induce large shifts in average values of some properties of the sample. To remove the larger crystallites from the sample, the synthesized nanoparticles were coated with oleic acid and dispersed in 10 ml of *n*-decane [6]. The larger nanoparticles sedimented from the suspension and were completely eliminated during centrifugation. For further analysis,

Table 1

List of synthesized samples and their properties.

Code	Reaction conditions		Size of nanoparticles		M ^c (Am ² /kg)	H _c (kA/m)	Fe/Ba ^d (J)
	T (°C)	Addition of oleic acid	Width (nm)	Thickness (nm)			
HF150	150	After ^a	9.6 ± 2.5 ^b	~3	0.7	3.2	12.06 ± 0.20
HF220	220	No	200–3000	~20	23.4	52	11.71 ± 0.41
OA240	240	Before ^a	11.7 ± 2.0 ^b	~3	1.4	24	11.84 ± 0.25
OA270	270	Before	120–140	~8	45.3	222	11.68 ± 0.27

^a After—oleic acid was adsorbed at the as synthesized nanoparticles; Before—oleic acid was added into the reaction mixture before the hydrothermal treatment.

^b Equivalent diameter of small, discoid particles measured on TEM micrographs.

^c Specific magnetization measured at 716 kA/m normalized per g of the nanoparticles. For the samples with adsorbed oleic acid the content of the organic phase was determined by thermogravimetry.

^d Ba/Fe ratio measured by using EDXS. The large platelet crystals of the sample HF220 served as standard.

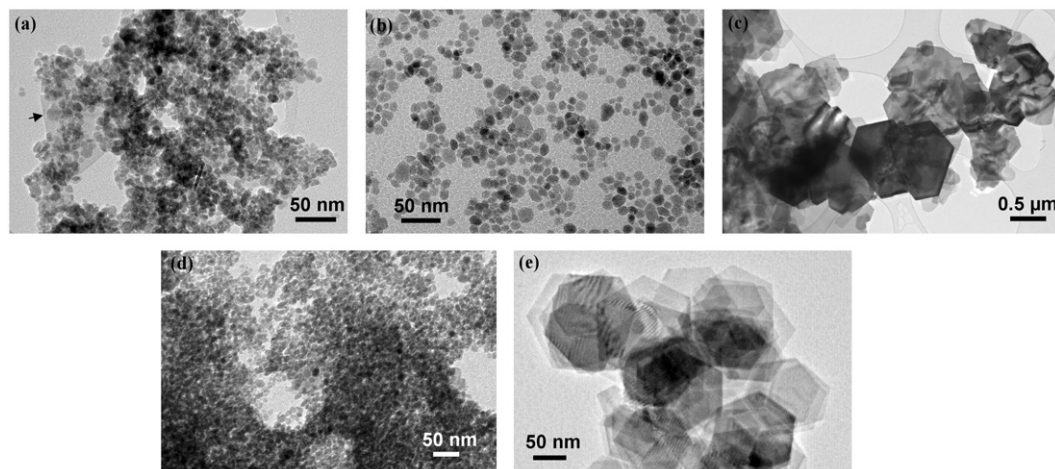


Fig. 1. TEM micrographs of the as-synthesized nanoparticles HF150 (a) and HF150 after dispersion and sedimentation of larger nanoparticles (b), the nanoparticles HF220 (c), OA240 (d), and OA270 (e).

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