

THE SYNTHESIS OF SUPERPARAMAGNETIC Ba-HEXAFERRITE PARTICLES

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Introduction

Submicron-grain-sized Ba-hexaferrite is one of the most commonly used materials in magnetic-recording applications [1] and one of the most promising materials in magnetic nanocomposites for the absorption of microwave radiation [2]. Up to now, when using chemical methods, a two-step procedure was always necessary and the thermal treatment was the final step in the preparation of submicron particles that were more or less agglomerated. There have been reports of some chemical routes, for example, glass crystallization [3] and hydrothermal synthesis [4,5], where the BaFe₁₂O₁₉ particles were synthesized in situ. In this contribution the synthesis of Ba-hexaferrite via co-precipitation at very low temperatures, i.e., below 100°C, will be reported.

Experimental

The starting materials for the syntheses were barium nitrate Ba(NO₃)₂ (Alfa, purity 97.2 %) iron nitrate Fe(NO₃)₃·9H₂O (Merck, purity 99.8 %), sodium hydroxide NaOH (Merck, purity 99.8 %) and deionized water. The hydrothermal syntheses were carried out in a 100-ml stainless-steel autoclave cell (Parr Instruments) with continuous agitation. The procedure began by dissolving an appropriate amount of barium and iron nitrate in the distilled water. The sodium hydroxide was then added to the solution. The molar ratio of the precursor [Ba²⁺]:[Fe³⁺] was optimized at 1:5 and the ratio of [OH⁻]:[NO₃⁻] was varied from 2/1 to 16/1. The concentration of Fe³⁺ was varied from 0.01 to 0.04 mol/L, while the Ba²⁺ was adapted to the ratio [Ba²⁺]:[Fe³⁺] = 1:5. Next, the autoclave was heated to the synthesis temperatures, T_s, which varied from 80°C to 140°C. The synthesis time t_s was 24 h. After the syntheses the products were washed with distilled water and HCl (0.1mol/L). The resulting samples were characterized with x-ray diffractometry (XRD), with a high-resolution TEM (HRTEM) and magnetic measurements (VSM).

Results and discussions

The co-precipitation of inorganic compounds is an ionic reaction in a solution where the precipitation of an insoluble compound, i.e., the target

compound, is the driving force. The nucleation of a precursor depends on the extent of the supersaturation. The increase of the concentration to a point where the saturation is exceeded will induce the nucleation. The nuclei formed might outgrow in stable nuclei and will then continue to grow. This is the case in Ba-hexaferrite, where the increase of the OH concentration will increase the concentration of the soluble [Fe(OH)₄]_nⁿ⁻ [6] complexes and thus increase the solute concentration and consequently reach the super saturation without using temperature and time as the crucial parameters to achieve the supersaturation. A high concentration of monomer BaFe₁₂O₁₂ leads to the formation of stable nuclei and further to small crystallites at low temperature. This reaction will be instantaneous. The variation of the morphology of the synthesized particles during the application of various temperatures was examined using the TEM. The monodispersed grain-size distribution was obtained below T_s = 120°C Fig. 1. Above this temperature, i.e., 80°C, a bimodal grain-size distribution results, Fig. 2. The synthesis time t_s was 24 h, which ensured that all the precursor in the autoclave was subjected to the dissolution-and-deposition process.

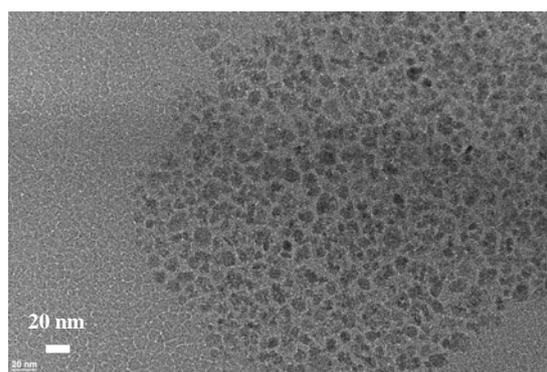


Fig. 1 TEM image of superparamagnetic particles of BaFe₁₂O₁₉ prepared at 80°C

There was enough time available for coagulation to proceed after 24 h of grain growth via diffusion of the dissolved solute. Below 120°C the activity of the side planes of the plate-like Ba-hexaferrite particles, which are characteristic for Ba-hexaferrite, decrease to the point where they are not

providing the coagulation. In this case there was a monomodal grain-size distribution, in spite of the fact that the sample was treated isothermally at for 24 h at 80°C.

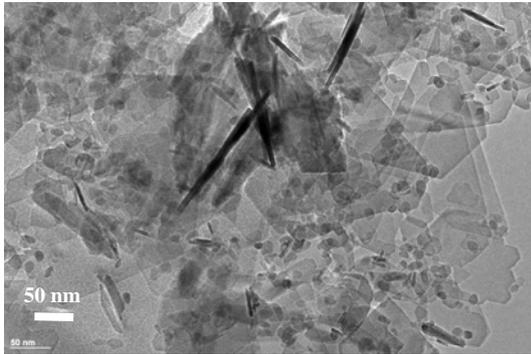


Fig. 2, TEM image of BaFe₁₂O₁₉ particles prepared at 140°C

In Fig. 1 the XRPD spectra of the samples synthesized at 140°C, 120°C, 100°C and 80°C for 24 h are shown. The positions of all the peaks correspond to the hexaferrite structure (PDF card No..). The shape and the relative intensities of the diffraction peaks differ in accordance with the particles' morphology. The (hkl) peaks (110, 220) are relative sharp, while the (hkl, where l ≠ 0) peaks are broader or even missing (for low l). The peaks originating from the lattice planes containing l-component are broader because of the very small dimensions of the crystal along the c-direction of the hexagonal structure, which corresponds to the thickness of the crystal. We must be aware that the thickness of the nanoparticles is only about 3 nm, which is less than 2 lattice dimensions along the c corresponding c-direction.

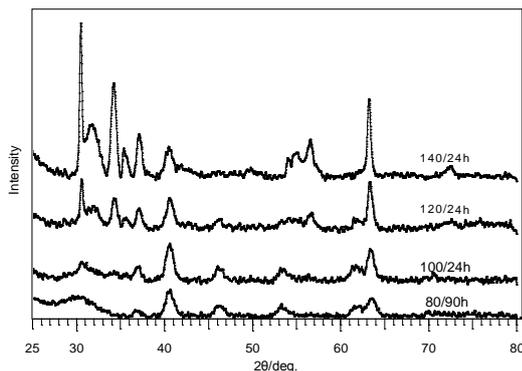


Fig. 3 XRPD spectra of BaFe₁₂O₁₉ powders prepared at 80°C, 100°C, 120°C and 140°C

In Fig. 4 the co-precipitated powder synthesized at 140°C exhibits hysteresis, while that synthesized below 120°C is superparamagnetic. The room-temperature magnetization of the samples synthesized below 120°C is around 3 emu/g, which is much smaller than the bulk value of 67.7 emu/g. The reduction of the magnetization of the magnetic particles with the decreasing particle size can be

caused by the incomplete coordination of atoms on the particle surface, leading to a noncollinear spin configuration, which causes the formation of a *surface spin canting* that might reduce the magnetization of the particles [7,8], and due to the thermal fluctuation of magnetic moments, which significantly diminishes the total magnetic moment at a given magnetic field.

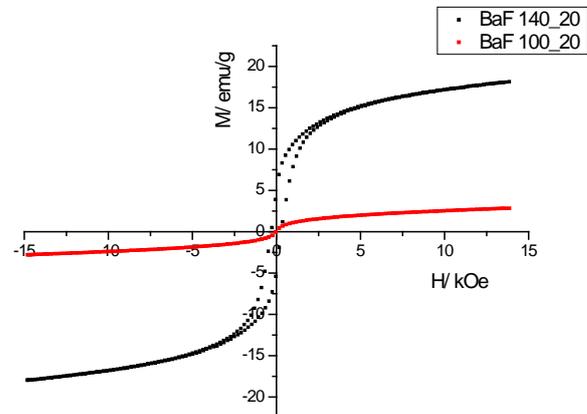


Fig. 4 Hysteresis of samples synthesized at 140°C and at 100°C

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