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Effect of annealing temperature on the structural and magnetic properties of barium hexaferrite powders prepared by a modified co-precipitation technique

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We report studies on the influence of the temperature of a high-temperature treatment on the microstructural and magnetic properties of nanosized single-domain $BaFe_{12}O_{19}$ powders synthesized by the modified co-precipitation method. The average particle size decreased from 90 nm to 25 nm as the synthesis temperature was decreased from 900 ºC to 800 °C; also, they did not exhibit the well-defined hexagonal shape that is characteristic for the hexaferrites. The value of the saturation magnetization M_s measured was very high, namely, 61.24 emu/g. The coercivity H_c of the powders ranged from 44 Oe to 103 Oe, which indicated that the particles were in a near-superparamagnetic state.

Keywords: hexaferrites, co-precipitation, magnetic properties, superparamagnetic.

INTRODUCTION

Barium hexaferrite ($BaFe_{12}O_{19}$) particles are widely used as permanent magnets, in microwave components and devices, such as circulators and absorbers, as well as a magnetic recording material, due to their unique characteristics, such as a high coercivity, a modest magnetic moment, a low or positive temperature coefficient of coercivity and an excellent chemical stability against environmental corrosion [1, 2]. The magnetic properties of powders of magnetic oxides are fundamentally related not only to their chemical composition, but also to the powders' particle size, crystal structure and morphology, which can vary depending on the preparation route. Conventional techniques for preparation of magnetic nano-particles include co-precipitation [3 ,4], microemulsion [5, 6], sol–gel auto-combustion processing [7, 8], mechano-chemical treatment [9], hydrothermal decomposition [10, 11], spark-plasma processing [12], aerosol pyrolysis [13], glass-ceramic route [14]. However, the particles prepared by these methods have a size of more than 100 nm. One of the reasons is that the hexaferrites are produced at high temperatures (above 1000°C), which leads to an uncontrolled growth of the particles and worsening of their size and shape homogeneity. It is, therefore, very important to find methods to reduce the synthesis temperature for preparation of single-domain nanosized hexaferrite particles with a size below 100 nm and with a high degree of homogeneity which concerns their size and shape. The most widely used method for synthesis of $BaFe_{12}O_{19}$ is co-precipitation; we present here a modified co-precipitation method − ultrasonically assisted co-precipitation, to produce single-domain nanosized powders of barium hexaferrite. When the solution is subjected to high-power ultrasound, bubbles are formed, grow, and implosively collapse. The collapse of bubbles caused by cavitation produces intense local heating and high pressures, with very short lifetimes. It also produces hot spots with effective temperatures of about 5000 K, pressures of 1000 atm, and heating and cooling rates above 1010 Ks^{-1} [15, 16]. This acoustic cavitation generates chemical reactions, in our case co-precipitation. We studied the influence of the high temperature treatment on the structural and magnetic properties.

EXPERIMENTAL

The $BaFe_{12}O_{19}$ powders were synthesized by modified co-precipitation induced by applying a high-power ultrasound wave (ultrasonically assisted co-precipitation). $Ba(NO_3)_2$ and $Fe(NO_3)_3$ were dissolved in deionized water in a molar ratio of Ba to Fe 1:10 due to the weak solubility of barium

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hydroxide in water ($10^{-3.6}$ at 25 °C) [17, 18, 19]. The co-precipitation was caused by adding NaOH at pH = 11.5. High-power ultrasound (Sonics ultrasonic processor 750 W) was applied to assist this process, which, as it is known, enhances the reaction rate, the mass transport and the thermal effects. The ultrasound wave with amplitude 40% was applied for 15 min, pulse on: 2 s, pulse off: 2 s. The precipitate was separated in a centrifuge, dried and milled. The precursor obtained was synthesized at 800 ºC (YLT1C), 850ºC (YLT1B) and 900 ºC (YLT1A) for 4 h.

The $BaFe_{12}O_{19}$ powders were characterized using X-ray diffraction analysis with Cu-K_α radiation and scanning electron microscopy (Philips ESEM XL30 FEG). The magnetic measurements were carried out at room temperature using a PPMS (Quantum Design) at a maximum magnetic field of 50 kOe. The magnetic measurements were conducted on a disoriented random assembly of particles.

RESULTS AND DISCUSSION

The XRD spectra of the samples exhibited the characteristic peaks corresponding to the $BaFe_{12}O_{19}$ structure only (Fig. 1).

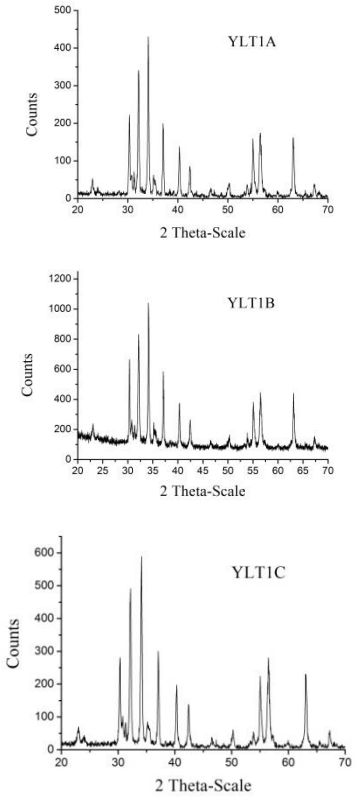

Fig. 1. XRD spectra of $BaFe_{12}O_{19}$ powders: (a) - YLT1A, (b) - YLT1B, (c) - YLT1C.

Scanning electron microscopy (SEM) was used to examine the grain size and morphology (Fig. 2). The average particle sizes of samples YLT1A, YLT1B and YLT1C were 90 nm, 66 nm and 25 nm, respectively (Table 1). The critical diameter for single-domain barium hexaferrite particles is about 460 nm [20], so that the particles were single domain in all powder samples. The particles were agglomerated due to the strong attractive magnetic force and high surface energy of the nanoparticles. The aggregation was strongest for sample YLT1C annealed at 800 °C with the smallest particle size. They did not exhibit the well-formed hexagonal shape that is characteristic for the hexaferrites, but rather an irregular shape between a sphere and a hexagonal platelet, similar to that obtained by single microemulsion technique [5] for particles with a size of less than 150 nm. The particles of sample YLT1C had a shape closer to the spherical. The process of forming the platelet shape typical for the $BaFe_{12}O_{19}$ hexagonal structure has not been completed due to the small particle size.

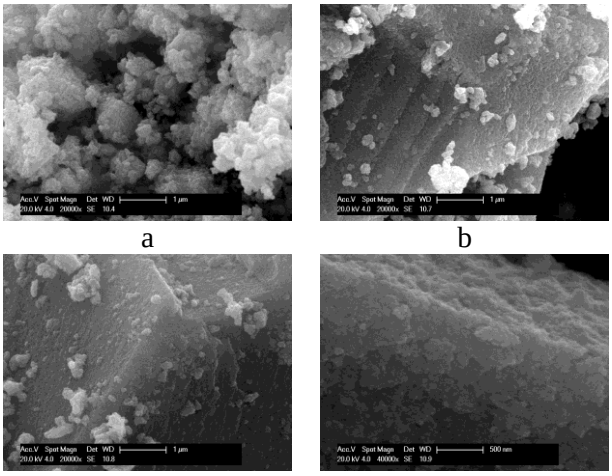

Fig. 2. SEM images of $BaFe_{12}O_{19}$ powders: (a) - YLT1A, (b) - YLT1B, (c, d) - YLT1C.

The hysteresis loops of the powders YLT1A, YLT1B and YLT1C at room temperature at a maximum applied field of 50 kOe are shown in Fig. 3 (a, c, e), respectively. Figs. 3 (b, d, f) show the hysteresis loops at low magnetic field. The magnetic parameters, namely, magnetization at magnetic field of 50 kOe (M_{max}), the remanent magnetization (M_r) and coercivity field (H_c) obtained from the hysteretic curves are given in Table 1. All samples did not reach the saturation magnetization despite the high magnetic field of 50 kOe. The maximum value for M_{max} of 61.24 emu/g at room temperature was measured for

Table 1. Properties of barium hexaferrite powders. *T* - high temperature synthesis, *D* - average particle size, M_s - saturation magnetization at 50 kOe (300 K), M_r - remanent magnetization (300K), H_c - coercivity field (300K).

Sample	*T*, °C	*D*, nm	M_{max}, emu/g	M_r, emu/g	H_c, Oe
YLT1A	900	90	61.24	7.54	44.06
YLT1B	850	66	50.85	8.68	59.06
YLT1C	800	25	48.97	11.17	103.17

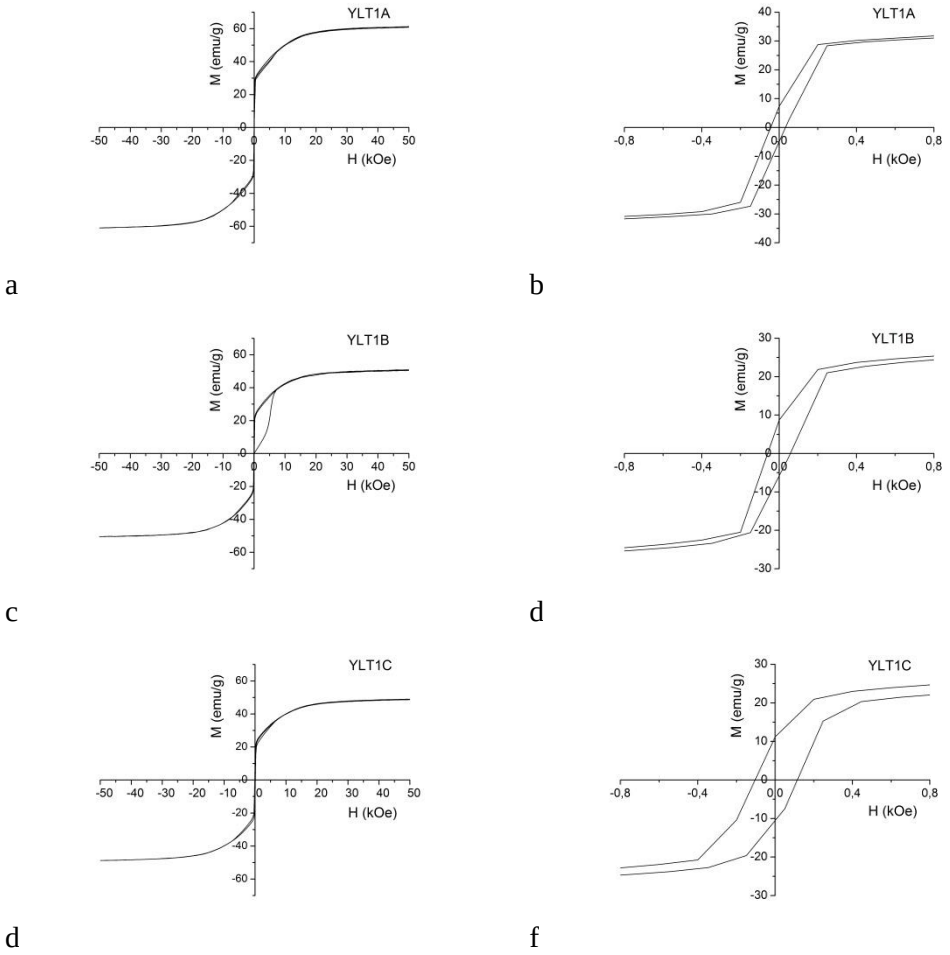

Fig.3. Hysteresis loops of (a, b) YLT1A, (c, d) YLT1B and (e, f) YLT1C samples.

sample YLT1A, which had the largest average particle size compared to the other samples. This value is very high, so that it can be expected that the saturation magnetization will be close to the theoretical values calculated for single crystal particles of barium hexaferrite, i.e. 72 emu/g, as reported by Shirk and Buessem [21].

The hysteresis loops for all samples were very narrow, which is not typical for hard magnetic materials like $BaFe_{12}O_{19}$. The coercivity H_c of powders was in the range 44 Oe − 103 Oe, which indicated that the particles were in a near-superparamagnetic state. For example, the coercivity of single crystal $BaFe_{12}O_{19}$ is 6.7 kOe [22, 23]. In the case of single-domain particles, the coercivity depends strongly on the particle size and shape, the degree of crystallinity, the magnetocrystalline anisotropy, the shape anisotropy etc. This lower value of coercivity is mainly due to the small particle size. It is interesting to note that H_c for the sample with the smallest particle size had the highest value − 103 Oe. This is probably due to the fact that despite the small size of the particles they are highly agglomerated as shown in Fig. 2c. This leads to pinning of the magnetic field at the boundaries of the particles in the agglomerates in a way similar to the domain-wall pinning in polydomain particles and, therefore, to increasing

the value of the coercive field of the sample compared to the field necessary in the case of a separate small particle.

CONCLUSION

An ultrasonically assisted co-precipitation technique for the synthesis of uniform barium hexaferrite particles was presented allowing one to obtain single-domain $BaFe_{12}O_{19}$ with particle size below 100 nm. The powders consist of particles with an irregular shape between spherical and plate-hexagonal. The particles with the average size of 25 nm have a quasi-spherical shape. The magnetization values of the powders at a magnetic field of 5 T may be attributed to the small particle sizes. The hysteresis loops for all samples are very narrow, which indicates that the particles are in a near-superparamagnetic state.

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ВЛИЯНИЕ НА ТЕМПЕРАТУРАТА НА СИНТЕЗ ВЪРХУ СТРУКТУРНИТЕ И МАГНИТНИТЕ СВОЙСТВА НА БАРИЕВ ХЕКСАФЕРИТ ПОЛУЧЕН ЧРЕЗ МОДИФИЦИРАН ПРОЦЕС НА СЪУТАЯВАНЕ

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(Резюме)

В настоящата статия се разглежда влиянието на температурата на синтез върху структурните и магнитните свойства на наноразмерен монодоменен $BaFe_{12}O_{19}$ получен чрез модифициран метод на съутаяване - ултразвуково съутаяване. Средният размер на получените частици намалява от 90 до 25 нм с понижаване на температурата на синтез от 900 ºС до 800 °С. Поради малкия си размер, частиците не са с добре изградена хексагонална форма, която е характерна за хексаферитите. Получените стройности на намагнитеността на насищане са много високи (61.24 emu/g). В зависимост от температурата на синтез, полето на коерцитивност H_c е в интервала 44 Oe - 103 Oe, което е индикатор, че частиците се намират в състояние близко до суперпарамагнитно поведение.