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The influence of the coprecipitation conditions on the low-temperature formation of barium hexaferrite

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Abstract We have investigated the formation of barium hexaferrite via the coprecipitation method. Various reagent salts and solvents were tested, and the coprecipitates were calcined at 300–800 °C for 1–50 h. The samples were characterized with X-ray powder diffraction, electron microscopy and magnetometry. The coprecipitation conditions had a significant influence on the formation time of the barium hexaferrite, which started to form at as low as 500 °C. The optimum coprecipitation conditions were: ethanol as a solvent and chlorides as reagent salts. Powders with optimum magnetic properties, saturation magnetization 60–63 emu/g and coercivity 4–5 kOe, were obtained by calcining at 600–700 °C.

Introduction

Barium hexaferrite and its derivatives can be used for permanent magnets, magnetic recording media and microwave applications. The best-known representative of the hexaferrite family has the chemical formula $BaFe_{12}O_{19}$ (BaM) and a magnetoplumbite structure [1]. Fine BaM powders exhibit suitable properties for magnetic recording media [2]. Finer starting powders also exhibit a superior sintering behaviour to coarser powders, resulting in lower sintering temperatures and denser ceramics [3]. This is of great advantage for permanent-magnet and microwave applications [4, 5].

Low-temperature formation of materials is necessary for energy saving. According to our preliminary studies [6, 7] the formation of BaM is possible at temperatures as low as 500 °C via coprecipitation from ethanol solutions. This is significantly lower than reported for the coprecipitation from water solutions [8–10] while other low-temperature methods are less convenient for scaling-up [11, 12]. Here we report on detailed studies of the influence of the coprecipitation conditions on the low-temperature formation of BaM.

Experimental procedure

Stoichiometric amounts of Ba and Fe salts—$BaCl_2$ (Ventron, ultrapure, Lot No. 044770307) or $Ba(NO_3)_2$ (Alfa Aesar, 99.995% metals basis, Lot No. 22331) and $FeCl_3$ (Alfa Aesar, 98%, anhydrous, Lot no. K05J02) or $Fe(NO_3)_3$ (Alfa, AR, Lot No. BA08255)—were dissolved in water or in alcohol solutions (75 vol.% of ethanol or isopropanol in water). The alcohol solutions are named for brevity “ethanol” and “isopropanol” in this manuscript. The Ba^{2+} and Fe^{3+} concentrations in the starting solutions (with pH ≤ 1) were 0.06 and 0.74 mol/l, respectively. Volumes of each solution were adjusted with respect to their concentration and stoichiometry. The obtained solutions of Ba–Fe salts were added to a NaOH solution (in water or in alcohols) with a pH of 13. After that the overall pH decreased, and then it was corrected to a minimum value of 13 with NaOH solution. The coprecipitation conditions we used are listed in Table 1. The slurry was filtered and the as-coprecipitated powders were washed with the 1 L of the same solvent as used during the coprecipitation (final washing step of the WETcl samples was accomplished with absolute ethanol), and dried overnight at 80–100 °C. The dried, coprecipitated precursors were calcined at 300–800 °C for 1, 10 or 50 h with heating and cooling rates of 10 K/min. The ETcl and the ISOcl calcinates were washed with water and then

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Table 1 Coprecipitation conditions

Sample	Reagent salts	Solvent
ETcl	Chlorides	Ethanol
ETni	Nitrates	Ethanol
ISOcl	Chlorides	Isopropanol
WETcl[a]	Chlorides	Water
Wcl	Chlorides	Water

[a] Final washing step with absolute ethanol

with absolute ethanol, before being filtered and dried. This was necessary to dissolve the NaCl, which has a limited solubility in alcohols and was a side product of the coprecipitation from chlorides with NaOH. WETcl and ETcl samples were additionally sintered at 1300 °C for 3 h.

The synthesis was monitored with X-ray powder diffraction (XRD) using a diffractometer with CuKα radiation (D4 Endeavor, Bruker AXS, Karlsruhe, Germany). The structure was refined and the crystallite size determined using a Rietveld refinement [13] and the Topas2R 2000 crystallographic program (Bruker AXS, Karlsruhe, Germany). A Rietveld refinement was also used to estimate the amount of amorphous phase. For this experiment we used 30 wt.% of high-purity corundum as an external standard. The results were verified with a standard XRD quantitative-phase-analysis approach using the same standard. The microstructures of the powders were observed using a scanning electron microscope (SEM, Jeol 840A) with Tracor Northern Analyzer for the energy dispersive analysis (EDS), and a transmission electron microscope (TEM, Jeol-2000FX). The magnetic properties of the calcined powders were measured using a magnetometer (Drusch & Cie Voltreg 1.4T) with a maximum magnetic field of 1.2 T and with a Quantum Design SQUID magnetometer with a maximum magnetic field of 5 T.

Results

In order to determine the optimum coprecipitation conditions for the low-temperature formation of BaM we designed a set of experiments in which we studied the influence of the solvent and the reagent salts (see Table 1). In each set of experiments only one of the studied parameters was varied with respect to the ETcl samples. The crystalline structures detected in the samples by the XRD analysis are listed in Table 2. The as-coprecipitated powders were amorphous with no distinctive XRD peaks. However, when they were exposed to air for several hours $BaCO_3$ crystallized from the amorphous Ba precursor and CO_2 (from the air). $BaCO_3$ was the only crystalline structure detected in the samples calcined below 500 °C. Despite very thorough washing of the coprecipitates NaCl was detected in the ETcl and ISOcl samples and was dissolved in water after the calcination (see "Experimental"). Up to 50 wt.% of amorphous phase was estimated with the quantitative XRD phase analysis in the samples calcined at 500 and 600 °C, and the amount of amorphous phase was found to decrease with temperature and time of calcination. The largest amount of amorphous phase was estimated in the ISOcl samples, and the lowest in the WETcl samples. BaM was first detected in the samples calcined at 500 °C (Fig. 1) when calcined for 10 h (WETcl and ETcl samples) and when calcined for only 1 h (ISOcl and ETni samples). The peaks corresponding to the BaM structure were indexed with the P63/mmc (194) space group. For the sake of clarity the indices were not added to Fig. 1 (see also Fig. 5). It should be noted that the γ-Fe_2O_3 peaks overlap with those of the BaM. Therefore, the presence of minor amounts of γ-Fe_2O_3 phase cannot be excluded from the powders calcined below 600 °C. Above this temperature, γ-Fe_2O_3 transforms to α-Fe_2O_3. In addition, other crystalline phases, $NaFeO_2$ and/or $BaFe_2O_4$, were detected in some of the samples.

Only in the ETcl samples calcined at minimum of 600 °C secondary structures were not detected. Their saturation magnetizations (Ms) of 60–63 emu/g measured with a SQUID at 5 T were in agreement with those reported for BaM prepared via coprecipitation from water at ≥800 °C [8, 9]. These samples consisted of nearly plate-like particles with diameters of 50–100 nm and thicknesses of 20–50 nm as is shown in Fig. 2. Only plate-like particles

Table 2 Crystalline structures detected with XRD in the calcined samples, where M stands for $BaFe_{12}O_{19}$, W for $BaCO_3$, α for hematite (α-Fe_2O_3), γ for maghemite (γ-Fe_2O_3), N for $NaFeO_2$ and B for $BaFe_2O_4$

Calc. temp. (°C)	Calc. time (h)	WETcl	ETcl	ISOcl	ETni
500	1	α	α, γ^*	M	W, M*
500	10	M, α	M, α^*	M	M
600	1	M, α	M	M	M, W
600	10	M, α^*	M	M, B*, N*	M, B*
700	1	M, α^*	M	M, B, N*	M, B*
700	10	M, α^*	M		M, B, α
800	1	M, α^*	M	M, B, N*	
800	10	M, α^*	M	M B, N	M, B, α^*

*Very low XRD intensity

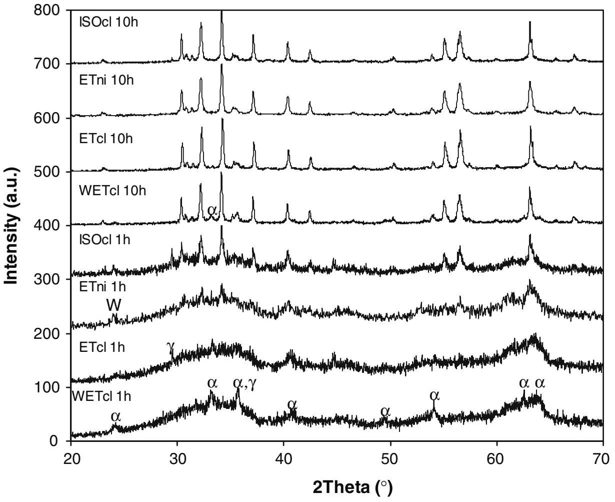


Fig. 1 X-ray diffractograms of the samples calcined at 500 °C for 1 and 10 h. α denotes α-Fe_2O_3, γ denotes γ-Fe_2O_3, W denotes $BaCO_3$ and non-marked peaks correspond to BaM

were observed with the TEM. In addition to that, the EDS analysis performed on the ETcl powders and on the sintered samples from the same powders revealed BaM as the only constituent phase with at.% Ba/Fe ~ 1/12. On the contrary, small Fe-oxide grains were observed with the SEM and detected with the EDS in the sintered WETcl samples. This is in full agreement with the XRD data (Table 1).

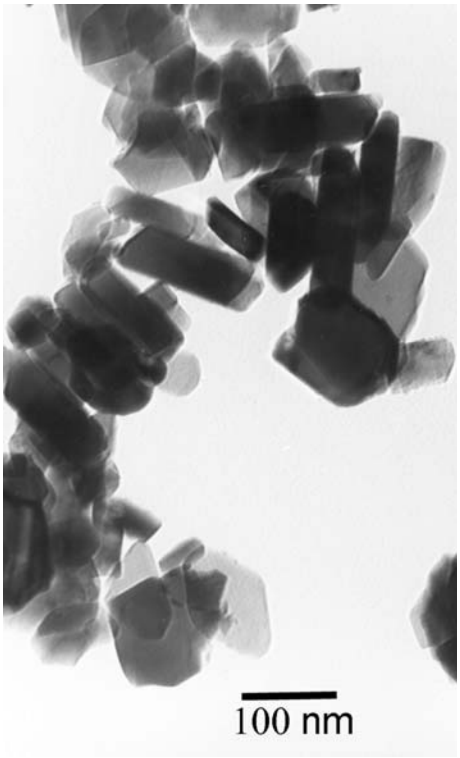


Fig. 2 TEM image of the single-phase ETcl sample calcined at 700 °C for 10 h

Figure 3 shows the magnetic properties of the BaM samples coprecipitated and calcined under different conditions. Note that the mean values of the measurements on 3–5 samples that were prepared under the same conditions are shown. The deviation from the mean measured value was maximum 10% for the samples calcined at 500 or 600 °C and maximum 4% for the other samples and was attributed to the measurement uncertainty. The values of the magnetization measured at 1.2 T ($M_{1.2}$) increased significantly up to 600 °C, and then only slightly with a further increase in temperature. This indicates that the crystallization of the BaM was completed, or nearly completed, up to 600 °C. The $M_{1.2}$ values of the ISOcl samples and of the ETni samples were lower than those of the ETcl samples. The maximum $M_{1.2}$ value, i.e., 57 emu/g, was measured for the WETcl sample calcined at 700 °C for 10 h. There was no significant difference between the $M_{1.2}$ values of the WETcl and of the ETcl samples. Similar dependence of the $M_{1.2}$ vs. calcination temperature was observed for the samples calcined for 1 h as for 10 h. It has to be noted that the BaM was not completely saturated at 1.2 T due to its high magnetocrystalline anisotropy (H_A = 1.7 T [1]). Therefore the $M_{1.2}$ values are not be mistaken with the Ms values ($M_{1.2}$ < Ms).

The coercivity (Hc) values increased in a similar way to the $M_{1.2}$ values. The Hc values exceeded 1,000 Oe in the ETcl and ISOcl samples calcined at 500 °C for 1 h, indicating the presence of BaM. Although a minor amount of γ-Fe_2O_3 structure could be present in the samples calcined below 600 °C, the contribution of the γ-Fe_2O_3 to the Hc value is negligible, since typical Hc values for γ-Fe_2O_3 are 50–100 times lower than that of BaM [1]. The maximum Hc values were obtained for the ISOcl samples calcined at a minimum of 500 °C, while for the other samples the increase in the Hc stopped at 600 °C. An additional minor increase in the Hc above these two temperatures can be attributed to an improvement in the BaM's crystallinity and an increase in the degree of shape anisotropy. The Hc is linearly dependent on the magnetocrystalline anisotropy (Ha) and the shape anisotropy (Hs) [2]. While the Ha is an intrinsic property, the Hs strongly depends on the morphology of the samples. In general, it increases with a decreasing particle size (down to the superparamagnetic limit). The average particle sizes determined with the XRD analysis for the samples calcined up to 700 °C were 70–95 nm for the WETcl samples, 65–90 nm for the ETcl samples, 65–80 nm for the ISOcl samples, and 50–70 nm for the ETni samples. This agrees well with the observed increase in the Hc values in the same direction. However, it has to be noted that the differences in the Hc values are only minor if we take into an account the deviation

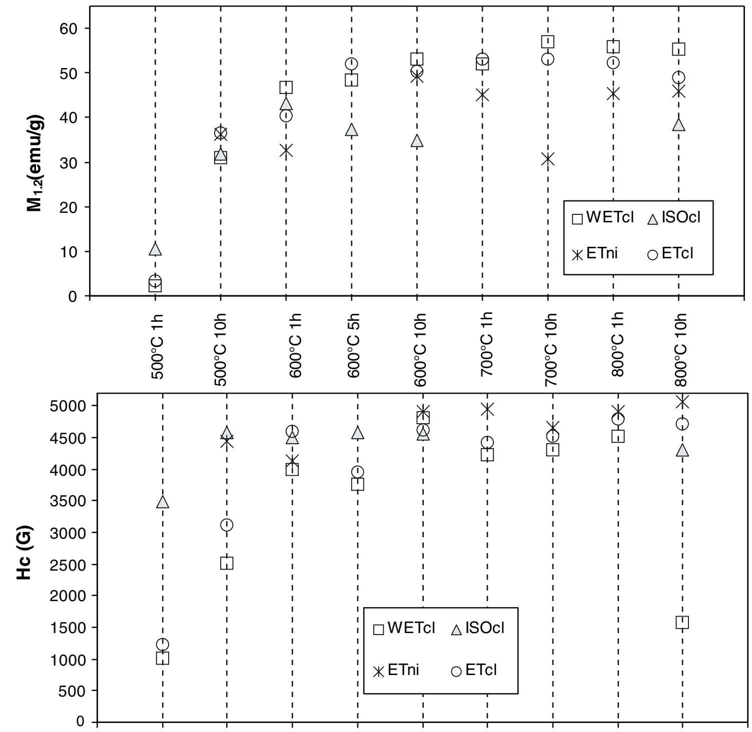


Fig. 3 Magnetization measured at 1.2 T ($M_{1.2}$) and coercivity (Hc) of the differently coprecipitated (Table 1) and calcined samples. The *x*-axis corresponds to calcination temperatures and times

between samples (maximum 11% for the samples calcined at 500 °C and maximum 5% for the others). The maximum Hc values reached 5,000 Oe, which is a typical value for BaM obtained with coprecipitation [8, 9]. The Hc values approach the Stoner–Wolfarth limit [14], indicating that the particles contain a single domain. This is also in accordance with the reported critical diameter for domain-wall formation in spheres [5]. The Hc decreased significantly for the WETcl samples, when calcined at 800 °C. This is a consequence of the particle growth, resulting in the formation of domains. Figure 4 shows electron micrographs of the WETcl samples calcined at 700 and 800 °C. Hexagonal platelets with diameters of around 100 nm can be observed in the sample calcined at 700 °C for 10 h. In the sample calcined at 800 °C for 10 h, larger particles can be observed in addition to the submicron particles. The largest particles are in the range of several tens of microns. The extensive particle growth at 800 °C is a consequence of the Ostwald ripening, due to an inhomogeneous particle size distribution of the coprecipitated precursors [15]. Larger particles grew at the expense of smaller ones, and domains can be formed in particles of this size, resulting in lower Hc values.

Discussion

The low-temperature formation of BaM was possible using the coprecipitation conditions reported here. The formation of BaM started at 500 °C (Fig. 1), which is significantly lower than the temperatures previously reported for coprecipitation methods [8–10]. During a typical solid-state formation of BaM the degradation of $BaCO_3$ results in the formation of an intermediate, $BaFe_2O_4$ [16]. In our case the BaM was formed directly, without the formation of $BaFe_2O_4$ in the ETcl and the WETcl samples and the formation of $BaFe_2O_4$ was not prevented in the ETni and in the ISOcl samples.

We showed that BaM is thermodynamically stable at 500 °C. However, the low Ms value of 55 emu/g (measured with a SQUID at 5 T) of the ETcl sample calcined at 500 °C for 50 h suggests that the crystallization was not completed in 50 h. Consequently, higher calcination temperatures (i.e., 600–700 °C) are suggested, in order to increase the kinetics instead of prolonging the calcination time at 500 °C. We have shown that it was possible to obtain single-phase BaM powders with a thorough washing of the ETcl coprecipitates followed by the calcination at ≥600 °C.

Due to secondary phases present in the ETni samples (Table 2) nitrates, as reagent salts, proved to be less favourable than chlorides. Minor amounts of secondary phases were detected also in some of the other samples. The presence of α-Fe_2O_3 indicates a minor deficiency of Ba. At high enough temperatures the α-Fe_2O_3 reacted with the leftover of Na (ISOcl samples) and formed $NaFeO_2$. The presence of both $NaFeO_2$ and $BaFe_2O_4$ in the ISOcl samples indicates an inhomogeneous distribution of Ba and

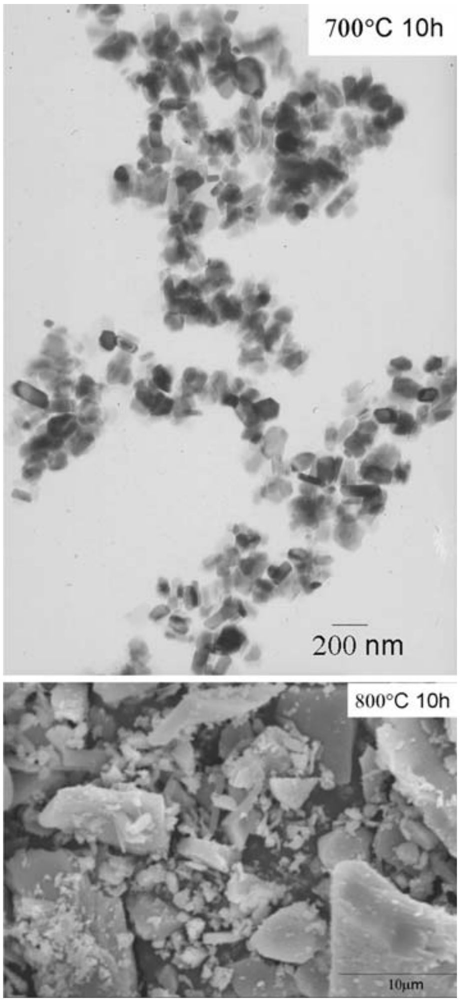


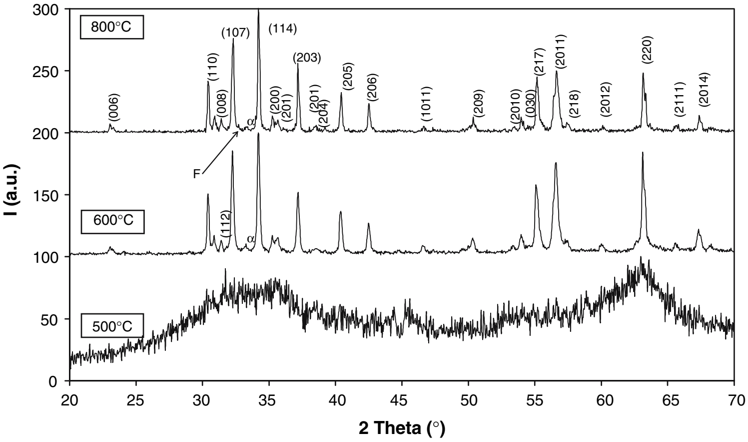
Fig. 4 TEM image of WETcl sample calcined at 700 °C for 10 h and SEM image of the sample calcined at 800 °C for 10 h

Fe in the coprecipitated powders. The probability of forming a $BaFe_2O_4$ with the Ba/Fe ratio of 1/2 is higher than the probability of forming a BaM with the Ba/Fe ratio of 1/12. Only ideal homogenization would result in the ideal distribution of Ba- and Fe-precursor species. This was obviously obstructed in the ISOcl samples either due to steric effects (long alcohol chains) or due to an increased diffusion distance (too much NaCl).

The homogeneity of the precursors can be also increased by the decreasing the probability of the formation of hard agglomerates during the drying of the coprecipitates. Alcohol chains adsorbed on the coprecipitated particles represent a steric effect and prevent strong agglomeration during drying, because only soft agglomerates are formed [17]. In contrast to this, particles coprecipitated from water are bonded with a much stronger hydrogen bond and strongly agglomerated (hard agglomerates). For a clear presentation, additional set of Wcl samples was prepared. These samples are prepared in the same way as the WETcl samples except that their coprecipitates were washed only with water. Figure 5 shows XRD diffractograms of the Wcl samples calcined for 10 h. In contrast to the other samples, no BaM peaks were detected in the sample calcined at 500 °C. Hematite peaks were detected in the other samples and a minor $BaFe_4O_7$ peak was detected in the sample calcined at 800 °C. This indicates that the precursors were less homogeneous than in the case of the WETcl and ETcl samples, resulting in an inhomogeneous distribution of cations and the consequent formation of $BaFe_4O_7$ (Ba/Fe ratio = 1/4 > 1/12 as for the BaM; see the discussion above). This is consistent with the expected poor reactivity of the hard agglomerated precursors coprecipitated from the water. Obviously, it was sufficient to use ethanol for the last washing of the coprecipitates (WETcl vs. Wcl samples) in order to prevent the formation of hard agglomerates and to decrease the formation temperature of BaM. This explains the lower temperature of the BaM formation in the WETcl samples when compared to the coprecipitation from chlorides used by others [8, 9].

The steric effect increases with the increasing length of the alcohol chain. In our case the steric effect increased in the direction of water < ethanol < isopropanol. The rate of

Fig. 5 X-ray diffractograms of the Wcl samples calcined for 10 h. The indices correspond to the $P6_3/mmc$ (194) space group (BaM), α denotes α-Fe_2O_3 and F denotes $BaFe_4O_7$



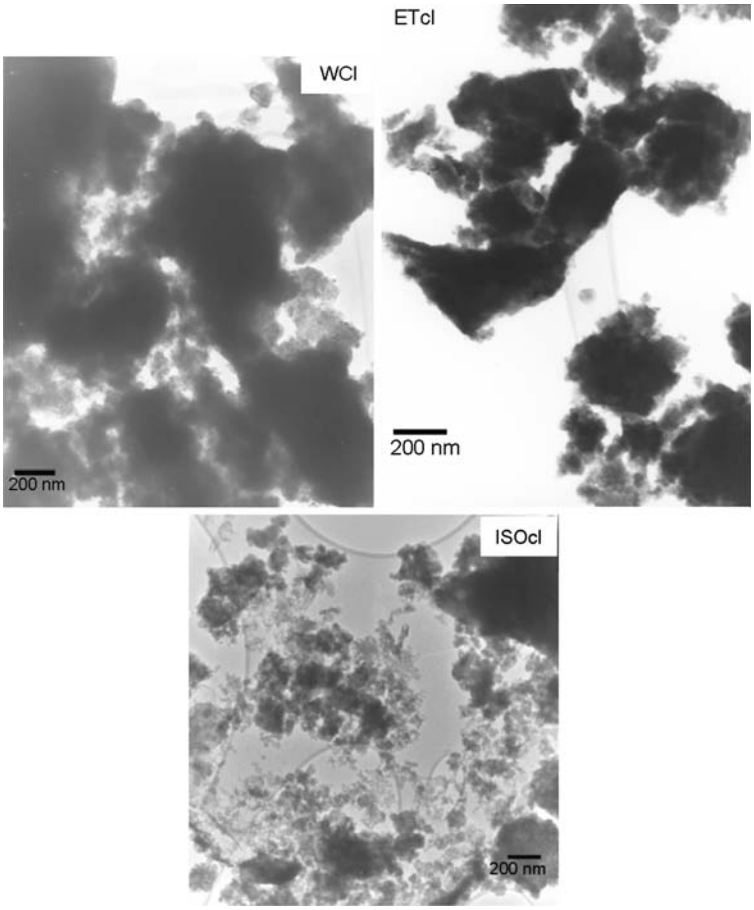


Fig. 6 TEM images of the as-coprecipitated samples

the agglomeration decreased in the same direction, as can be seen from the TEM images of the different coprecipitates shown in Fig. 6. This explains the fastest formation of BaM at 500 °C in the ISOcl samples (Table 2, Figs. 2, 3). Due to the problems associated with the isopropanol that were discussed above ethanol is preferred as a solvent.

Conclusions

The formation of $BaFe_{12}O_{19}$ using various coprecipitation conditions was studied. The type of solvent and the reagent salts influenced both the formation temperature and time of the $BaFe_{12}O_{19}$. The $BaFe_{12}O_{19}$ began to form at 500 °C. The optimum conditions for the low-temperature formation of $BaFe_{12}O_{19}$ were as follows: ethanol as a solvent for the coprecipitation and chlorides as the reagent salts. The optimum calcination temperature with respect to the kinetics of the formation and the magnetic properties was 600–700 °C.

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