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Nonconventional methods for obtaining hexaferrites
II. Barium hexaferrite

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Abstract

Small particles of barium hexaferrite ($BaFe_{12}O_{19}$) were synthesized by thermal decomposition of precursors obtained by a new coprecipitation method. The influence of precursors' history upon their thermal behavior and phase composition evolution were investigated. © 1998 Elsevier Science B.V.

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1. Introduction

Among the different classes of magnetic materials, hexagonal hard ferrites such as barium ferrite have attracted much attention because of their potential application in permanent magnets, microwave devices and magnetic recording media [1–3].

Fine particles of such ferrites cannot be produced easily and routinely by the conventional mixed oxide ceramic method (which involves the calcination of a mixture of $BaCO_3$ and α-Fe_2O_3 at ca. 1200°C). Under such conditions, wet chemical methods are nowadays used for achieving this goal. Correspondingly, we developed some precursor's methods – which consist in obtaining solid precursors of mixed oxides, in which the metallic ions present in a proper ratio are already mixed at atomic scale. We reported in a previous work some results concerning the obtaining of lead hexaferrite [4].

This paper presents our results about the synthesis of fine barium hexaferrite, using as precursors some hydroxy-oxalate coprecipitates. Special emphasis is given on the influence of precursors' history upon their thermal behavior.

2. Experimental

The mixed oxide's precursors were obtained by a chemical coprecipitation technique. So, dilute NH_4OH or NaOH solutions (25% w/w) were added to the suspensions of iron oxalate ($FeC_2O_4.2H_2O$, reagent grade) and a barium salt ($Ba(CH_3COO))_2{\cdot}2H_2O$ or $Ba(NO)_2$, reagent grade). The copre-

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cipitations were performed at pH∼12, and at room temperature. The coprecipitates were then filtered off and washed with water.

The composition of the precursors was determined by quantitative analysis: the metal content by gravimetric technique, and the carbon, hydrogen and nitrogen contents by using a combustion method coupled with chromatographic techniques.

In order to characterize the precursors as well as their calcination products, IR spectrometry, X-ray diffraction, thermal analysis and magnetic measurements were applied.

The IR spectra were recorded with a BIO-RAD FTIR 1255 spectrophotometer type.

The X-ray diffractograms were recorded with a DRON 3 X-ray diffractometer with CoK_α radiation.

The heating curves (TG-DTG-DTA) were obtained by using Paulik–Paulik–Erdey type Q-1500 derivatograph, in static air, at various heating rates. Samples weighing 100 mg were used. In order to record the DTA curves, α-alumina was used as inert material.

The magnetic properties (the saturation magnetization) at room temperature of the final decomposition products were determined by means of permeameter method.

3. Results and discussion

3.1. Precursors

Although slight modification of the synthesis conditions lead to changes of the chemical composition of the synthesized precursors, the following general formulas may be written for the compounds obtained with the two precipitating agents:

(a) for the case of the precipitation with NaOH

$$[m'\mathrm{Fe(Ox)}n\,\gamma\text{-FeOOHBa(Ox)(H}_2\mathrm{O)}_{24-x}]$$

where $m'+n=10.5$; 11; 11.5; 12 and $0<x<12$.

(b) for the case of the precipitation with NH_4OH solution

$$(\mathrm{NH})_4[m\mathrm{Fe(Ox)Ba(Ox)(H}_2\mathrm{O)}_{24-n}]$$

where $m=10.5$; 11; 11.5; 12 and $0<x<12$.

The IR spectra pointed out that all the four precursors are present in the structural skeleton of $FeC_2O_4{\cdot}2H_2O$ The precursors obtained during the precipitation with NaOH solution contain a reduced amount of oxalate anions (approximately half). This statement is supported qualitatively by the decrease in intensities corresponding to the IR bands of oxalate anions and quantitatively by chemical elemental analysis. The remaining amount of iron is present as γ-FeOOH (IR analysis confirmed the identification), the synthesis conditions being favorable to a partial oxidation of the Fe^{2+} ions. Traces of γ-FeOOH were also identified in the first type of precursors. (∼3–5%)

From the crystallinity point of view, the two types of precursors are very different. While amorphous solids are obtained by precipitation with NaOH, crystalline ones are obtained in the case of precipitation with NH_4OH solution. In the latter, the X-ray diffraction data pointed to the presence of a mixture consisting of two well-crystallized phases: monoclinic iron oxalate $FeC_2O_4{\cdot}2H_2O$ (ASTM 23-293) and triclinic barium oxalate $BaC_2O_4{\cdot}3H_2O$ (ASTM 23-67). A higher crystallinity was found for the precursors with $BaNO_3$ as starting material. The crystalline phases are characterized by broad diffraction lines indicating small particles. The mean crystallite sizes, calculated by Sherer' [5] formula from the four most intense diffraction lines, vary in the 250–300 Å range.

3.2. Nonisothermal and isothermal analyses of the precursors

As the investigated compounds represent precursors for mixed oxides, the goals of the nonisothermal and isothermal investigations are:

– to determine the temperature range of occurrence and the stoichiometry of the thermal transformations; and
– to establish how the history of compounds may influence their thermal behavior and quality of the final mixed oxide.

The investigated precursors undergo decompositions in several steps (5–6), the final decomposition temperatures for all studied compound being close to 900°C. No phase transformations were in evidence. Due to their comparable composition and structure, the thermal transformations of the precursors obtained during the precipitation with the same agent occur with similar stoichiometry in the same temperature

Table 1
Thermal analysis of the investigated precursors

Precursor	T_i–T_f [a]/°C	Mass loss/%	Thermal effect	Assignment
$Ba(CH_3COO)_2$–FeC_2O_4	58–100	3.86	endo	humidity water release
(NH_4OH)	100–180	17.09	endo	NH_4OH and lattice water release
	180–308	28.00	exo	decomposition of iron oxalate to γ-Fe_2O_3
	408–510	1.04	exo	decomposition of barium oxalate to barium carbonate
	660–835	1.47	exo	reaction in solid state between iron oxide and barium carbonate, formation of barium hexaferrite
	Total:	51.46		
$Ba(NO_3)_2$–FeC_2O_4	55–104	2.41	endo	humidity water release
(NH_4OH)	104–170	14.37	endo	NH_4OH and lattice water release
	170–286	29.38	exo	decomposition of iron oxalate to γ-Fe_2O_3
	407–502	1.18	exo	decomposition of barium oxalate to barium carbonate
	687–850	1.76	exo	reaction in solid state between iron and barium carbonate, formation of barium hexaferrite
	Total:	49.10		
$Ba(CHCOO)_2$–Fe_2O_4	72–152	3.89	endo	two step water release
(NaOH)	152–200	3.31	endo	
	200–300	9.30	exo	decomposition of iron oxalate
	404–503	1.90	exo	decomposition of barium oxalte to barium carbonate
	545–662	1.23		reaction in solid state between iron oxide and barium carbonate, formation of barium hexaferrite
	662–722 [b]	041	exo	
	722–861	1.79	exo	
	Total:	21.83		
$Ba(NO_3)_2$–FeC_2O_4	68–149	4.54	endo	two step water release
(NaOH)	149–211	4.58	endo	
	211–316	8.38	exo	decomposition of iron oxalate
	410–500	1.80	exo	decomposition of barium oxalate to barium carbonate
	533–631	1.02	exo	reaction in solid state between iron oxide and barium carbonate, formation of barium hexaferrite
	631–737 [b]	0.90		
	737–888	1.74	exo	
	Total:	22.96		

[a] T_i – initial temperature of thermal transformation, T_f - final temperature of thermal transformation.
[b] Continuous mass loss.

range. Table 1 summarizes the thermogravimetric obtained data for the investigated precursors (Fe/Ba ratio 12).

The nonisothermal analysis was associated with IR spectra and X-ray diffraction investigation for a complete and reliable assignment of thermal transformations. Hence, the following mechanism may be accepted:

– The first two decomposition reaction steps accompanied by endothermic effects represent the release of humidity water and NH_4OH, bonded lattice water.
– These reactions are followed by the oxidative decomposition of the iron oxalate present in the precursors and dehydration of γ-FeOOH to iron oxide. The phase analysis showed the existence of two phases: barium oxalate and iron oxide γ-Fe_2O_3. The XRD patterns recorded for the two types of precursors show a low crystallinity for the compounds obtained by precipitation with solution of BaOH, while

a high one is shown for the second type of precursors.

– The next thermal transformation which occurs practically in the same temperature range, respectively 400–500°C, consists in the decomposition of barium oxalate into barium carbonate. The phases discerned in the intermediates are $BaCO_3$ and iron oxides: γ-Fe_2O_3 as main products and α-Fe_2O_3 in traces (4–7%). Although all the intermediates are crystalline, a better crystallinity is put into evidence for the precursors obtained by precipitation with NH_4OH.

– The following thermal transformations are due to the transformation of γ-Fe_2O_3 into α-Fe_2O_3 as well as to the reaction between iron oxides and $BaCO_3$ leading to mixed oxides. The thermogravimetric curves put into evidence for the two types of precursors reveal a different progress of these solid state reactions.

3.2.1. *Precursors obtained by precipitation with NH_4OH solution*

The TG curve levels off in the 510–660°C (raw material $Ba(HCOO)_2$) and 502–687°C (raw material $Ba(NO_3)_2$) ranges. The X-ray patterns of the intermediates obtained at 550°, 600°, and 650°C inidcate the tendency of a gradual conversion of γ-Fe_2O_3 into α-Fe_2O_3. The transformation is complete at the temperature corresponding to the beginning of the mass loss. A single decomposition step is recorded in the 660–835°C (raw material $Ba(HCOO)_2$) and 687–850°C (raw material $Ba(NO)_2$) ranges. In these temperature ranges, α-Fe_2O_3 reacts with $BaCO_3$ to form monoferrite $BaFe_2O_4$, which reacts further on with α-Fe_2O_3 to form hexaferrite. The first diffractions line corresponding to barium hexaferrite were detected at 750°C.

3.2.2. *Precursors obtained by precipitation with NaOH solution.*

The TG curves reveal two distinct reaction steps. In the first reaction step, which occurs in the 540–607°C (raw material $Ba(CHCOO)_2$) and 533–631°C (raw material $Ba(NO_3)_2$) ranges, an amount of 36 and 28%, respectively, from $BaCO_3$ content is decomposed. The phase analysis put into evidence the formation of $BaFe_2O_4$. Simultaneously, weak lines corresponding to barium hexaferrite were also evidenced. One can advance two main reasons for the increased reactivity of the solid intermediates namely; the partially amorphous nature of the intermediates and a better mixing at molecular level of the cations, due to a advanced destruction of the initial raw materials structure.

This reaction is followed by a continuous mass loss, in the 607–722°C (raw material $Ba(NO_3)_2$) range. γ-Fe_2O_3 is detected even at the beginning of the second well-defined decomposition step (~10%). The presence of this oxide at such a high temperature is due to the low degree of crystallinity of the samples. Similar conclusions were referred to by Macieas et al. [6].

Although the literature data [7–11] mentioned an exothermic effect associated with ferrite formation at ~750°C, it was not found in our case, due to the overlapping of the ferritization reaction with the decomposition of the precursors (e.g. decomposition of $BaCO_3$).

At the final decomposition temperatures the residue contain three crystalline phases, respectively: barium hexaferrite ($BaFe_{12}O_{19}$), barium monoferrite ($BaFe_2O_4$), and iron oxide (α-Fe_2O_3).

In order to obtain a pure barium hexaferrite the decomposition residues were submitted to further isothermal treatments for intervals of time ranging from 1 h to 30 h at 900°C. The phase analysis of the end products outlines the following reaction between $BaFe_2O_4$ and α-Fe_2O_3, when hexaferrite was obtained faster in the residues obtained from the precursors precipitated with NaOH solution. If, for this reaction, the amount of monoferrite is already consumed after 20 h annealing, for the other two, the diffraction lines characteristic for monoferrite are present even after 30 h of calcination at this temperature. Working with a molar ratio Fe/Ba=12, constant small amounts of α-Fe_2O_3 impurity phase (~9–11%) remained in the calcination residues even after an annealing time of 30 h.

In order to get a single phase sample the initial Fe/Ba ratio was slightly decreased. The pure hexaferrite was obtained at a value of the ratio which equals 10.5, in this condition the ferritization being complete after 20 h of calcination. The mean crystallite size of the obtained hexaferrite varies in the 420–470 Å range.

In Fig. 1 the IR spectra of the decomposition intermediates, obtained in the decomposition of the precursor on precipitation with NaOH solution (raw

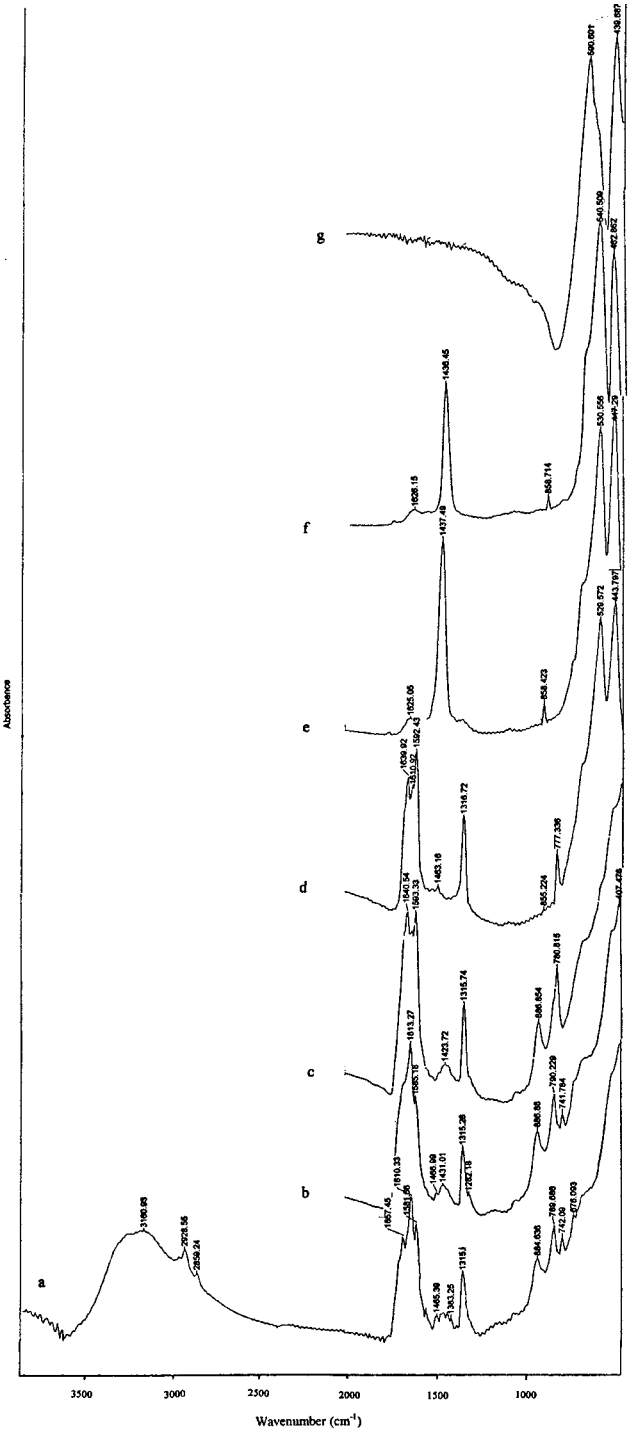

Fig. 1. IR spectra of the precursor (precipittaion with NaOH raw materials FeC_2O_4–$Ba(CHCOO)_2$) and its decomposition intermediate. (a) Intial precusor; (b) intermediate obtained at 200°C; (c) intermediate obtained at 300°C; (d) intermediate obtained at 400°C; (e) intermediate obtained at 500°C; (f) intermediate obtained at 700°C; and (g) intermediate obtained at 900°C (20 h calcination).

material $Ba(CH_3COO)_2$), are given. The vibration assigned to the stretching modes of water and hydroxyl ions were put into evidence in the 2800–3400 and 676 cm^{-1} ranges. These bands disappeared at temperature close to 200°C due to the loss of water molecules. The presence of the oxalate anion was put into evidence through the band present in the 1657–740 cm^{-1} range. The pattern successively changed above 200°C until 500°C indicating its total decomposition. In the temperature range of 500–850°C, carbonate intermediates were isolated, which exhibit a very strong band at ~1430 cm^{-1} characteristic of the presence of CO_3^{2-} anion. The band disappeared at the completion of the reaction (900°C). After the decomposition of iron oxalate, strong absorption bands, due to the iron–oxygen bonds, (corresponding to iron located in octahedral and tetrahedral position respectively), were observed in the 540–540 cm^{-1} range. The slight shift of the bands position connected with the changes in their intensities ratio are due to the transformation of iron oxides into hexaferrite during heating.

The measured value of the saturation magnetization for the obtained barium hexaferrite was 47.58 emu/g lower than the literature value of 71 emu/g [12]. A study concerning the optimization of the magnetic properties will be carried out later.

4. Conclusions

1. New precursors of barium hexaferrite synthesized by an original method have been chemically and physico-chemically characterized.
2. The relation between precursors' history, thermal behavior and phase composition of the decomposition intermediates was investigated
3. Although the decomposition behavior was mostly the same for the two types of precursors, differences were observed in the solid state formation reaction of barium hexaferrite.
4. The proper ratio for the composition $BaO.nFe_2O$ (n=5.25) was found in order to get single phase barium hexaferrite with a mean crystallite size in the 420–470 Å range.

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