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NON-CONVENTIONAL METHODS FOR OBTAINING HEXAFERRITES

Thermal analysis of some precursors

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Abstract

The thermal behaviour of the polynuclear coordination compounds $[Fe_{12-x}Sr(malic)_{19-1.5x}]\cdot 18H_2O$ and $[Fe_{12-x}Sr(gluc)_{19-1.5x}]\cdot 20H_2O$ precursors of strontium hexaferrite was investigated, and a decomposition mechanism is proposed. A pure hexaferrite with a mean crystallite size value of about 250 Å was obtained after 5 h calcination at 800°C of the gluconic precursor (x=1.5).

Keywords: non-conventional methods, strontium hexaferrite, TG–DTG–DTA

Introduction

The synthesis of fine nanometric particles of mixed oxides by a 'precursor' method knows a large utilization in obtaining this kind of materials. Polynuclear coordination compounds precursors represent efficient precursors for the synthesis of fine particles of mixed oxides of spinelic and perovskitic type [1]. The major advantages of this procedure are the following: (i) uniformity of oxides nanoparticles with high surface; (ii) chemical homogeneity on atomic scale; (iii) high chemical purity and strain free without grinding. Their use in hexaferrite synthesis has not been reported till now. The main difficulty consists in obtaining the coordination compound precursor, which has to contain the two metals in a ratio of $12Fe^{3+}:1M^{2+}$ (where M^{2+}=Ba, Sr, Pb).

This problem can be solved by choosing a ligand which can generate anorganic polymeric chains due to its capacity to form bridged bonds between two metallic ions.

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Among the ligands which fulfill this conditions the polyhydrocarboxylic acid have to be mentioned.

Following our research on small hexaferrite particles [2, 3], this paper reports the synthesis and thermal behavior of polynuclear coordination compounds precursors of strontium hexaferrite for the first time.

Experimental

The synthesis method of the polynuclear compounds

The synthesis method of the polynuclear compounds represents a version of Melson and Pickering one [4]. The polynuclear coordination compounds were separated from the reaction medium (a solution containing Sr(II)-Fe(III)-polyhydrocarboxylic acid, either malic or gluconic) by extraction with ethanol. For a complete precipitation 24 h and a repeated adjusting of the pH to 5.5–6 by adding a 20% NH_4OH solution were necessary. The products were filtered, washed with ethanol and dried. The metal ratio Fe/Sr of the synthesized polynuclear coordination compounds varies in the range 10.5:1 to 12:1.

IR measurements

IR measurements were obtained by the KBr disc technique in the range 400–4.000 cm^{-1} using a BIO-RAD FTIR 125 infrared spectrophotometer type.

Thermal measurements

Thermal measurements were performed with a Q-1500 D Paulik-Paulik-Erdey derivatograph in a static air atmosphere, at heating rates in the range 5–10°C min^{-1}. The sample mass was 100 mg.

X-ray diffractograms

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

Magnetic susceptibility measurements

Magnetic susceptibility measurements of the residual oxides were performed by using a Faraday balance with $Hg(SCN)_4$ as calibrant.

Results and discussion

Non-isothermal analysis of the precursors

On the basis of the analytical data, the formula of the synthesized compounds are:

$$[Fe_{12-x}Sr(malic)_{19-1.5x}]\cdot 18H_2O$$

$$[Fe_{12-x}Sr(gluc)_{19-1.5x}]\cdot 20H_2O$$

where $0<x<1.5$ and (malic) and (gluc) are the dianion of malic and gluconic acid. The thermogravimetric curves are shown in Figs 1 and 2. For a complete and reliable assignment of the thermal transformations the non-isothermal analysis was associated with IR spectra and X-ray diffraction measurements.

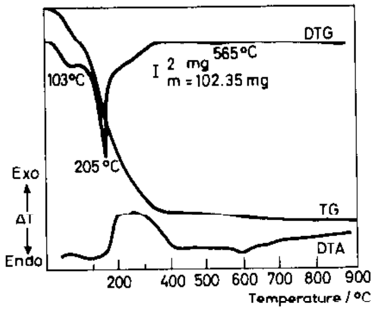

Fig. 1 Thermoanalytical curves of $[Fe_{12-x}Sr(malic)_{19-1.5x}]\cdot 18H_2O$ (heating rate 5°C)

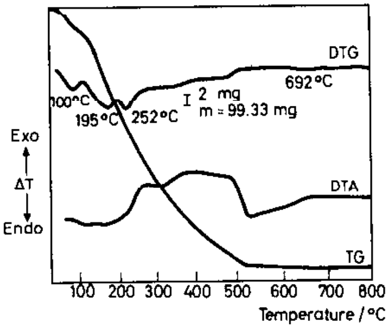

Fig. 2 Thermoanalytical curves of $[Fe_{12-x}Sr(gluc)_{19-1.5x}]\cdot 20H_2O$ (heating rate 5°C)

Hence, the following decomposition mechanism can be assumed for the first polynuclear coordination compound:

$$Fe_{12-x}Sr(malic)_{19-1.5x}]\cdot 18H_2O \xrightarrow{80-144^{\circ}C} [Fe_{12-x}Sr(malic)_{19-1.5x}] \xrightarrow{144-260^{\circ}C}$$

$$Fe_{12-x}Sr(CO_3)_{19-1.5x} \xrightarrow{260-377^{\circ}C} Fe_{12-x}Sr(CO_3)O_{18-1.5x} \xrightarrow{558-688^{\circ}C}$$

$$Fe_{12-x}SrO_{19-1.5x} \tag{1}$$

The temperatures above the arrows correspond to the temperature of decomposition occurrence at 5°C min^{-1} as recorded by DTG curve.

The endothermic dehydration is followed by two strong exothermic processes in the temperature range 144–377°C, namely the thermal degradation of the malic ligand with formation of a carbonate and its conversion to the oxocarbonate intermediate $[Fe_{12-x}Sr(CO_3)O_{18-1.5x}]$. This intermediate is stable up to 558°C when in an endothermic reaction CO_2 is evolved. On the DTA curve, a relatively weak exothermic peak is observed (maximum at 718°C), which can be associated with the ferritization reaction.

For the second polynuclear coordination compound a five stepped decomposition may be proposed:

$$[Fe_{12-x}Sr(gluc)_{19-1.5x}]\cdot 20H_2O \xrightarrow{91-150^{\circ}C} [Fe_{12-x}Sr(gluc)_{19-1.5x}] \xrightarrow{150-228^{\circ}C}$$

$$[Fe_{12-x}Sr(tartric)_{19-1.5x}] \xrightarrow{228-292^{\circ}C} [Fe_{12-x}Sr(oxalic)_{19-1.5x}] \xrightarrow{292-560^{\circ}C}$$

$$Fe_{12-x}Sr(CO_3)O_{18-1.5x} \xrightarrow{678-800^{\circ}C} Fe_{12-x}SrO_{19-1.5x} \tag{2}$$

The decomposition starts with an endothermic dehydration followed by a second endothermic step (150–228°C) assigned to formation of the tartaric anions due to the breaking of some internal bonds of the gluconic ligand. The next temperature range (228–560°C) is characterized by the change of the tartaric intermediate to oxocarbonate one $Fe_{12-x}Sr(CO_3)O_{18-1.5x}$, via oxalate compound.

In this case the ferritization occurs simultaneously with the decomposition of the precursor (e.g. $SrCO_3$ decomposition into SrO). The overlapping of these two reactions led to a wide exothermic peak on the DTA curve with the maximum at 778°C.

One has to mention the low temperature range in which $SrCO_3$, formed as intermediate decompose, namely 558–688/678–800°C for $[Fe_{12-x}Sr(malic)_{19-1.5x}]\cdot 18H_2O$/$[Fe_{12-x}Sr(gluc)_{19-1.5x}]\cdot 20H_2O$ compounds. A two stepped decomposition in the range 800–1000°C is reported in literature [5]. Such a behavior may be attributed to an increased reactivity of the solid intermediates.

The phase analysis performed on the reaction intermediates of both precursors obtained at 550, 600, 650 and 700°C showed the existence of three crystalline phases, namely γ-Fe_2O_3, α-Fe_2O_3 and $SrCO_3$. The increasing temperature indicates the consumption of $SrCO_3$ and a gradual transformation of γ-Fe_2O_3 into α-F_2O_3. The transformation is complete at about 700°C. If strontium hexaferrite phase begins to appear at temperatures higher than 700°C due to the reaction between γ-Fe_2O_3 (or α-Fe_2O_3) and SrO in the case malic precursors, for gluconic ones it is formed directly from and iron oxides and $SrCO_3$ phases.

Oxide products

The phase composition of the calcination residia was found by using X-ray diffraction as well as magnetic data. The mean size of crystallites have been evaluated by using Sherrer formula [6] for the main XRD intensities (higher than 10 relative intensity). Before the comments concerning the obtained results one has to mention that in all the investigated residia the X-ray diffraction lines belonging to SrO have not been identified. This is probably due to the low crystallite sizes which are dispersed in the residia.

In order to get a pure well crystallized hexaferrite, the decomposition residia were submitted to further isothermal treatments for intervals of time ranging from 1 to 5 h at 800°C. Data concerning the residual decomposition products of the two precursors, each with two different metalic ratio, namely Fe/Sr 12:1 and 10.5:1 are presented in Table 1.

Table 1 Structural data of the oxid residia obtained after a calcination of 1 and 5 h at 800°C

Precursors		Hexaferrite				α-Fe_2O_3			
		content/%		d*/Å		content/%		d/Å	
		1 h	5 h	1 h	5 h	1 h	5 h	1 h	5 h
$[Fe_{12-x}Sr(malic)_{19-1.5x}]\cdot 18H_2O$									
	x=0	–	7	–	320	100	93	490	315
	x=1	29	52	284	256	71	48	342	245
$[Fe_{12-x}Sr(gluc)_{19-1.5x}]\cdot 20H_2O$									
	x=0	47	52	211	298	53	16	298	261
	x=1.5**	78	100	257	243	20	–	243	–

* mean crystallite size

** traces of $SrCO_3$

The content of hexaferrite is higher in the residue obtained from the precursors with gluconic ligand, it increases with the duration of calcination and decreases with the ratio Fe/Sr. A pure hexaferrite is obtained after a calcination of 5 h at 800°C of the gluconic precursor with x=1.5.

Preliminary magnetic measurements performed at room temperature, indicate a magnetization of 48 emu erg^{-1} for this precursor. The obtained value is lower than the saturation value reported in literature [7]. Measurements at nitrogen liquid temperature are going on.

It is important to emphasize two features of the obtained mixed oxide:

a) the values of the mean crystallite sizes which vary in the range 211 Å <d<320 Å:

b) the temperature of a complete ferritization is lower than most of the temperatures mentioned in literature [7–11].

Conclusions

1. A new procedure for the synthesis of some polynuclear coordination compounds precursors of strontium hexaferrite was developed.

2. The thermal behaviour of $[Fe_{12-x}Sr(malic)_{19-1.5x}]\cdot 18H_2O$ and $[Fe_{12-x}Sr(gluc)_{19-1.5x}]\cdot 20H_2O$ compounds were investigated, and a decomposition mechanism was suggested.

3. A pure hexaferrite with a mean crystallite size value of about 250 Å was obtained after a calcination of 5 h at 800°C of the gluconic precursor (x=1.5).

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