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COBALT FERRITE FROM CITRATE PRECURSOR BY SELF-PROPAGATING COMBUSTION REACTION

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Abstract

Cobalt ferrite was synthesised by the thermal decomposition of a citrate precursor through a novel self-propagating combustion reaction (SPCR) and the progress of this reaction is explained. Cobalt ferrite obtained by this reaction is compared with the products obtained by heat treatment of the citrate complex. The thermal behaviour and structures of the precursor, the synthesised ferrite, and the other decomposition products are investigated.

Keywords: citrate complex, cobalt ferrite, self-propagating combustion reaction

Introduction

New Chemi-Douce [1–3] routes for synthesis of cobalt ferrite and other magnetic materials are being continuously investigated [4]. Some of these techniques include sol–gel [5], metal oxide chemical vapour deposition [6], co-precipitation [7], microemulsion [8], by hydrolysis in polyol medium [9] and decomposition of the precipitates prepared from non-aqueous precipitation routes [10]. These methods are employed for producing precursor powder with an intimate mixture of initial constituents so as to require lower calcination temperature. Here, the critical factor can be evaporation of solvents due to inhomogenity and formation of segregation phases. The coprecipitation route can suffer, moreover from impurities due to the precipitating agents, alteration of stoichometry due to incompleteness of the precipitation process, and loss of material during the repeated washing steps. The sol–gel route, on the other hand, has many preparation steps, requires expensive chemicals, and is also a time-consuming process [11]. The polyol technique has the limitation of choosing a particular nucleating agent, and the medium for growth of the particles, and involves growth of mostly spherical particles. The precipitation technique [10] gave nanosized γ-Fe_2O_3 particles, but involved more reaction steps. Also in any of these synthetic routes the use of thermal analysis techniques is sparingly used. Knowledge of the formation of the final product from its precursor through the use of thermal analysis techniques has gained importance in the understanding the synthesis of materials and compounds [12–14].

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In the present investigation we report the synthesis of monophasic cobalt ferrite ($CoFe_2O_4$) through a self-propagation route employing a citrate precursor. This synthetic route can be considered interesting for its simplicity, reproducibility and easy scale-up. It produces a homogenous precursor with a controlled stoichometry and also does not require expensive chemicals. It is a low-energy reaction and can be carried out in a china dish in an open atmosphere. In this self-propagation combustion reaction, a suitable oxidant/fuel for our study was found to be polyethylene glycol. In our earlier studies we have successfully used this oxidant/fuel for the synthesis of ultrafine gamma ferric oxide particles from different precursors [15–16].

To understand the effect of heat treatment of the citrate precursor without the help of any fuel/oxidant, we have also carried out the thermal analysis study of this citrate precursor in air atmosphere. The present study envisages the use of employing thermal analysis techniques in the synthesis of the cobalt ferrite.

Experimental

Polyethylene glycol of molecular mass 4000 employed in the present study was obtained commercially, and the other chemicals employed were analar grade.

Preparation

The monophasic cobalt ferrite ($CoFe_2O_4$) was prepared according to the process schematically represented in Fig. 1. Stoichometric proportions of ferrous ammonium sulphate and $CoCl_2{\cdot}6H_2O$ were dissolved in the minimum volume of water and 15.0 mL of 0.1 M citric acid was then added as a complexing agent. Care was exercised in adjusting the pH (~6) of the solution by cautiously adding ammonia solution. After constant stirring for sometime, a homogenous precipitate was obtained. The whole solu-

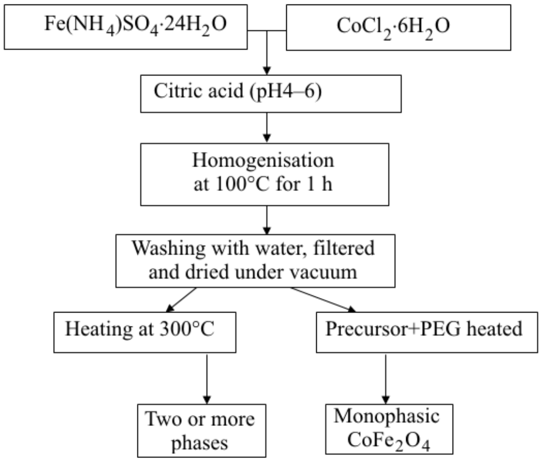

Fig. 1 Schematic representation for synthesis of cobalt ferrite

tion was concentrated by heating to 100°C for 1 h for homogenisation to take place. The precipitate was then washed with water till the filtrate was free from excess chloride, sulphate and citric acid. The precipitate was then dried in vacuum. This citrate precursor hereafter is called CM_1.

The sample CM_1 was then divided into two portions. One portion was heated in air at 300°C for 2 h in a silica crucible, and cooled to room temperature. This residue is called CM_2. The CM_2 sample was later characterised for its structure and thermal behaviour.

Another portion of the precursor (CM_1) was mixed with polyethylene glycol in the mass ratio of 1:5 and ground together in a pestle and mortar. The resultant mixture was placed in a silica crucible and heated in air. During heating, the polyethylene glycol melts, froths, and finally ignites to form a dark brown residue, this residue is called CM_3. This reaction is called the self-propagating combustion reaction [16–17], as the reaction proceeds with self-propagation to give the required final product. The reaction is exothermic and is fast (completes within 2–3 min), the exact temperature of the reaction is not possible to determine. However, on observation with thermocouple placed near the sample indicated that the highest temperature reached in the present case is ~500°C. The thermal behaviour of the self-propagation reaction in the synthesis of other ferrite materials is presented in our other communication [17–18].

Characterization

Thermal traces were obtained from Mettler Toledo Star instruments, under air atmosphere, with a heating rate of 10°C min^{-1} in silica boats. The X-ray diffraction patterns were obtained employing a Geol JDX-8P spectrometer using CuK_α radiation. The infrared spectra were recorded on a Perkin Elmer model 337 spectrometer.

Results and discussion

Thermal analysis

The TG/DTA traces of CM_1, CM_2 and CM_3 samples respectively are shown in Figs 2a–c. The TG trace of sample CM_1 in Fig. 2a showed a multistep mass loss. The first mass loss of ~3.5% started from the room temperature and went up to 200°C. The second step mass loss (~4.5%) occurred from 200 to 400°C and finally a mass loss of 7.6% from 450 to 670°C was observed. The DTA trace in Fig. 2a showed a small endotherm at 50°C, a very broad endotherm up to 400°C, and an exotherm at 620°C. The TG trace of CM_2 in Fig. 2b showed a multistep mass loss. The first mass loss of 2% started from 30°C and ended at 130°C, the second mass loss of about 2.5% started from 200°C and ended at 480°C, and the final mass loss of about 2.5% started at 490°C and ended at 750°C. The DTA trace in Fig. 2b showed a small exotherm at 460°C and a small endotherm at 640°C. Figure 2c showed only a mass loss of 1.5% on the TG trace for CM_3 and an endotherm on the DTA trace at 100°C. Broad and weak endotherms were also observed around 660°C.

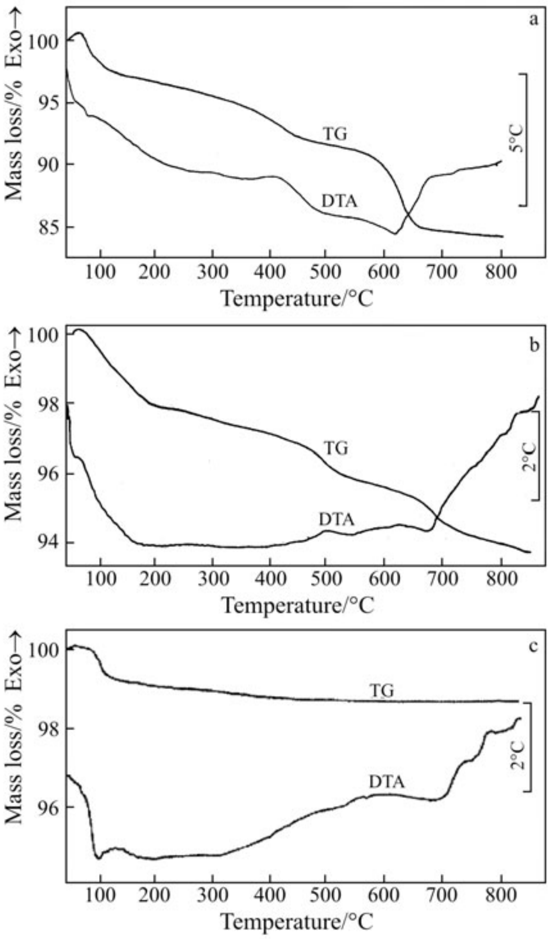

Fig. 2 TG/DTA trace of the a – CM_1, b – CM_2 and c – CM_3 samples

The first step of mass loss observed in Fig. 2a, was slow and continued up to 200°C, suggesting the loss of adsorbed water molecules. In the second step a partial decomposition of the citrate complex took place. The partial decomposition of the citrate complex was also verified from the elemental and the infrared spectral studies carried out after heating sample CM_1 at 440°C, for 2 h. The exotherm at 400°C in the DTA trace for CM_1 sample in Fig. 2a corresponds to an oxidative decomposition of this sample. The final mass loss step was quite slow initially, and later showed a steep mass loss which finally reached a plateau at 670°C. Elemental analysis of the sample obtained by heating sample CM_1 at 670°C for 2 h did not show any presence of carbon. Hence the endotherm at 620°C indicated further decomposition of the partially decomposed sample to form monophasic $CoFe_2O_4$. The infrared spectra of this heat-treated CM_1 sample to 670°C for 2 h (shown in Fig. 3) had peaks corresponding only to ferrite frequencies [19], i.e., at 445 and 550 cm^{-1}. Figure 4a shows the X-ray

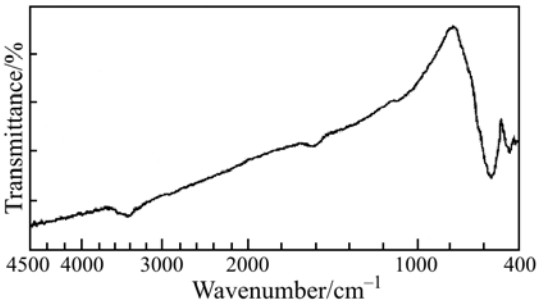

Fig. 3 Infrared spectra of the CM_1 sample

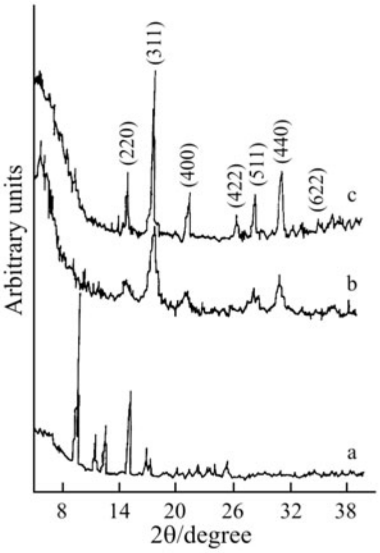

Fig. 4 X-ray diffraction pattern of the a – CM_1, b – CM_2 and c – CM_3 samples

diffraction pattern of the CM_1 sample. This diffraction pattern shows that the sample CM_1 is crystalline with the presence of the peaks (<20° in the 2θ values). The X-ray diffraction pattern of the sample heated to 670°C for 2 h resembles a monophasic $CoFe_2O_4$ as given in the literature [22].

To understand the thermal behavior of the CM_2 sample, the TG/DTA trace of this sample was obtained and is shown in Fig. 2b. The multi-step mass loss observed on the TG trace suggested a slightly different thermal behaviour when compared with the CM_1 sample shown in Fig. 2a. The mass loss of 2.0% in the first step indicated the loss of adsorbed water. The second mass loss stage was observed to be slow and continuous indicating the further partial decomposition of the CM_2 sample. The partial decomposition of the citrate complex is supported by the elemental and the infrared spectral studies carried out on the sample CM_2 to 400°C, for 2 h. The DTA trace also showed a small exothermic peak at 460°C, indicating a partial decomposition of the

Table 1 Information about the thermal behaviour of the CM_1, CM_2 and CM_3 samples

Sample code	TG						DTA	
	1st step		2nd step		3rd step		Endo	Exo
	Temp. range/°C	Mass loss/%	Temp. range/°C	Mass loss/%	Temp. range/°C	Mass loss/%	Peak temp./°C	Peak temp./°C
CM_1	30–440	7.8	450–670	7.6	–	–	50 (weak) 400 (weak and broad) 620	400
CM_2	30–130	2.0	200–480	2.5	490–750	2.5	640	460
CM_3	80–180	1.5	–	–	–	–	100; 660 with shoulders	–

CM_2 sample. The third step of mass loss corresponds to the final formation of monophasic $CoFe_2O_4$. This is also observed as an endotherm on the DTA trace at 640°C. The X-ray pattern of CM_2 in (Fig. 4b) showed broad reflections corresponding to partially decomposed citrate complex. The infrared spectrum and the X-ray diffraction pattern of the heat-treated CM_2 sample at 750°C in air for 2 h resemble the results for the residue obtained by giving heat treatment to CM_1 sample at 670°C for 2 h. It is observed from the two thermal traces i.e., Figs 2a and b, that the heat-treated sample CM_2, behaves differently when compared to the thermal behaviour of the CM_1 sample. It may be inferred here that $CoFe_2O_4$ is obtained only at higher temperature from the citrate complex when carried out under normal heating.

The TG trace of the CM_3 sample showed only a 1.5% mass loss from 80 to 150°C for the dehydration of the adsorbed water and after this step, the trace showed no change in mass. The DTA trace showed an endotherm peak at 100°C, for the dehydration step. Moisture plays an important role in the formation and stabilisation of synthesised ferrites [12, 20], Though the presence of the moisture in the form of adsorbed water molecules was necessary, the properties of the ferrites are enhanced on desorption of these water molecules [21]. The results observed on the above thermal traces for the three samples are summarized in Table 1. The X-ray diffraction pattern of the sample CM_3 is shown in Fig. 4c, this pattern matches with that of the monophasic $CoFe_2O_4$ as given in the literature [22]. The X-ray diffraction pattern of this sample CM_3 (possessing monophasic $CoFe_2O_4$) shown in Fig. 4c is indexed accordingly. The sample CM_3 has cubic symmetry with a space group FD3m and lattice parameter of 8.40 Å.

Conclusions

The following conclusions are drawn from these investigations:

- Self-propagating combustion reactions can be conveniently employed for synthesis of ferrites, and specifically for a monophasic cobalt ferrite of commercial composition.
- Cobalt ferrite can be obtained from the thermal decomposition of a citrate complex under controlled conditions and at higher temperatures.
- Understanding of the thermal behaviour of the precursor was found essential for obtaining the required ferrite.
- The presence of adsorbed water molecules stabilizes the metastable ferrite.

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