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Precursor combustion synthesis of nanocrystalline cobalt substituted nickel zinc ferrites from hydrazinated mixed metal fumarates

S.G. Gawas, V.M.S. Verenkar *

Department of Chemistry, Goa University, Taliegao Plateau, Goa 403206, India

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ABSTRACT

In present investigation, a systematic approach towards synthesis of nanocrystalline ferrites, $Co_xNi_{0.6-x}Zn_{0.4}Fe_2O_4$ ($x = 0.1$ and 0.4) has been reported by room temperature decomposition of precursors, $Co_xNi_{0.6-x}Zn_{0.4}Fe_2\ (C_4H_2O_4)_3 \cdot 6N_2H_4$ ($x = 0.1$ and 0.4). The precursor complexes were characterized by Fourier transform infrared spectroscopy (FTIR), chemical analysis and thermal studies like isothermal mass loss, total mass loss, thermogravimetry (TG), derivative of thermogravimetry (DTG) and differential thermal analysis (DTA). The TG–DTG–DTA patterns of both precursors reveal multistep decomposition with complete ferritization at 410 °C. The thermally decomposed products were characterized by X-ray diffractometry (XRD) for phase purity. The FT-IR spectroscopy studies of the same shows complete removal of all organic moieties from decomposed precursors. The nanophasic nature of synthesized ferrites was confirmed by transmission electron microscopy (TEM) analysis as well as from broadening of XRD peaks. The AC magnetization studies show the existence of single domain and superparamagnetic particles, which supports nanosize particles distribution in the ferrite system under study.

1. Introduction

The research in synthesis of nanocrystalline materials with desired geometry, size and stoichiometry is increasing day by day due to different properties they show than the bulk. Actually, the composition, cation distribution and particle size and shape are the important factors responsible for deviation in structural and magnetic properties [1–4] thereby opening doors of newer applications in various areas of interest such as sensing of toxic gases, medical field and in catalysis as magnetically recoverable catalyst for organic transformation [5–8]. Materials, especially magnetic ferrites are gaining attention of research groups from different fields due to their application from nanometric scale to bulk. Ferrites are known to posses high resistivity and low eddy current loss which suites their candidature for higher frequency applications [9,10]. The hunger for achieving desired characteristics in ferrites has led to development of new synthetic strategies as well as improvement in the existing ones. Various instrumental and traditional wet chemical methods namely; combustion [11], sol-gel [12–14], coprecipitation [15,16], spray pyrolysis [17], hydrothermal synthesis [18], reverse micelle [19,20] and precursor [21–47] have been successfully employed for synthesis of nanocrystalline ferrites with compositional control and size uniformity. Among these methods, the precursor method is extensively explored by using different carboxylates like citrates [21], malates [22], oxalates [23,24] etc., which involves decomposing of metal carboxylates in furnace above 400 °C to form nanocrystalline ferrite powder. Moreover some metal carboxylate precursors, coordinated with hydrazine has been found to undergo low temperature decomposition to metal oxides [25–49]. The present study describes systematic investigation towards synthesis of one such precursor namely, hydrazinated mixed metal fumarate and its decomposition to corresponding nanocrystalline ferrites and also the role of hydrazine in auto-decomposition of precursors.

2. Experimental

2.1. Synthesis

The hydrazinated mixed metal fumarates were synthesized by adding aqueous mixture of metal chlorides to sodium fumarate–hydrazine hydrate mixture, stirred for 2 h in N_2 atmosphere. The requisite amount of all the metal chloride mixture (except ferrous chloride) was prepared in aqueous medium while ferrous chloride solution was prepared fresh from iron powder and conc. HCl under CO_2 atmosphere. The analytical grade chemicals were used for synthesis. The yellow precipitate formed was filtered, washed with ethanol and dried with diethyl ether under suction. The above

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* Corresponding author. Tel.: +91 832 6519321; fax: +91 832 2452886.
E-mail address: vmsv@rediffmail.com (V.M.S. Verenkar).

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Table 1
Metal content and hydrazine analysis of $Co_xNi_{0.6-x}Zn_{0.4}Fe_2\ (C_4H_2O_4)_3{\cdot}6N_2H_4$ (x = 0.1 and 0.4).

Composition x	Mass%									
	Nickel		Cobalt		Zinc		Iron		Hydrazine	
	Obs.	Calc.	Obs.	Calc.	Obs.	Calc.	Obs.	Calc.	Obs.	Calc.
0.1	4.22	4.15	0.82	0.83	3.66	3.69	15.63	15.79	27.24	27.15
0.4	1.52	1.66	3.18	3.33	3.66	3.70	15.63	15.79	27.56	27.15

procedure was repeated to precipitate both the complexes and can be represented as follow.

$$MCl_{2(aq)} + 2FeCl_{2(aq)} + 3Na_2C_4H_2O_{4(aq)} + 6N_2H_4{\cdot}H_2O(aq) \rightarrow MFe_2(C_4H_2O_4)_3{\cdot}6N_2H_{4(S)} + 6NaCl_{(aq)} + 6H_2O_{(l)}\ (M = Co^{2+}, Ni^{2+}, Zn^{2+})$$

2.2. Characterization

The hydrazinated mixed metal fumarate complexes were analyzed for their stoichiometry based on standard methods of analysis. The FT-IR studies of the precursors and their decomposed end products were carried out on a FTIR Shimadzu IR Prestigue-21 Spectrophotometer, to confirm the presence of different organic moieties and their linkage with metal ions in the complexes. The hydrazine content was chemically analyzed by volumetric analysis using 0.025 M KIO_3 as titrant under Andrew's condition [50]. Different metal content in precursor complexes were determined by titrating with EDTA, after decomposing the known amount of precursor in concentrated HCl followed by separation on column [50,51]. The simultaneous thermogravimetric (TG), derivative of thermogravimetry (DTG) and differential thermal analysis (DTA) measurements of the precursor were recorded from RT to 810 °C on a NETZSCH STA 409 PC (Luxx) analyzer. The experiments were carried out in dry air at a purge rate of 60 mL per min and ramping rate of 10 °C per min with 10-15 mg of the samples in alumina cups. The isothermal mass loss and total mass loss studies of the precursors were also carried out at different pre-determined temperature based on TG-DTA results. The structure and phase purity of the thermally decomposed end product of the precursors were studied using Rigaku Mini flex X-ray diffractometer with monochromatized Cu Kα radiation filtered through Ni absorber. The morphology was studied by transmission electron microscopy, taken from Philip's-CM20 electron microscope. The AC susceptibility measurements were carried out on DOSE AC susceptibility Setup standardized with Nickel, operating at 5000Oe and supplied by ADEC Embedded Technology and Solutions Pvt., Ltd., Corlim, Goa.

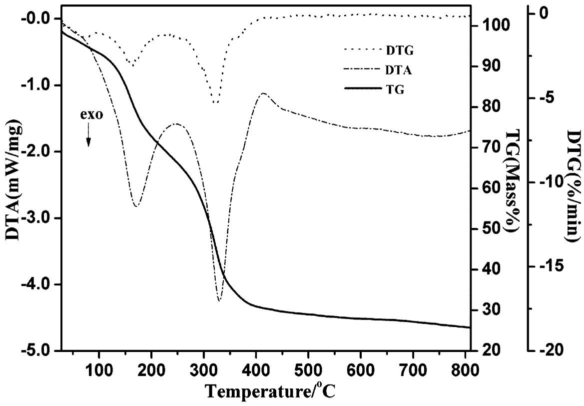

Fig. 2. TG–DTG–DTA plot of $Co_{0.1}Ni_{0.5}Zn_{0.4}Fe_2\ (C_4H_2O_4)_3{\cdot}6N_2H_4$.

2.3. Thermal decomposition of the hydrazinated fumarate precursors

The precursor complexes were uniformly spread in a ceramic clay dish and lighted with burning splinter. The precursor catches fire and a red glow that subsequently formed spreads immediately over the entire bulk to give auto-combusted nano-sized particles of $Co_xNi_{0.6-x}Zn_{0.4}Fe_2O_4$. These $Co_xNi_{0.6-x}Zn_{0.4}Fe_2O_4$ powders were further heated in air in a furnace at 450 °C for 5 h to remove any residual carbon formed during the decomposition of complexes and termed as "as prepared" ferrites in the following text.

3. Results and discussion

3.1. Chemical analysis and FTIR studies

The percentage content of different metals and hydrazine in precursors has been tabulated in Table 1. The stoichiometry has been assigned as, $Co_xNi_{0.6-x}Zn_{0.4}Fe_2(C_4H_2O_4)_3{\cdot}6N_2H_4$ (x = 0.1 and 0.4) based on the observed percentage of hydrazine, cobalt, nickel, zinc and iron which matches closely with the calculated values. The FTIR spectrums of both precursor complexes (Fig. 1) are identical and almost superimposable. Complexes show four bands in the region 3190–3353 cm^{-1} which are characteristic of N—H stretching frequencies. The observed N—N stretching frequencies

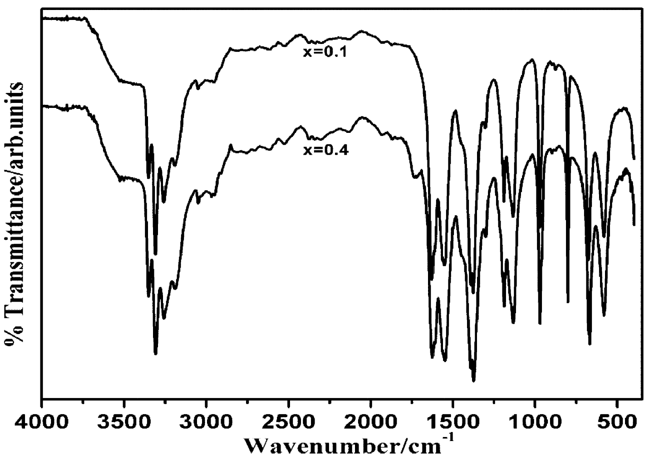

Fig. 1. FTIR spectra of $Co_xNi_{0.6-x}Zn_{0.4}Fe_2\ (C_4H_2O_4)_3{\cdot}6N_2H_4$ (x = 0.1 and 0.4).

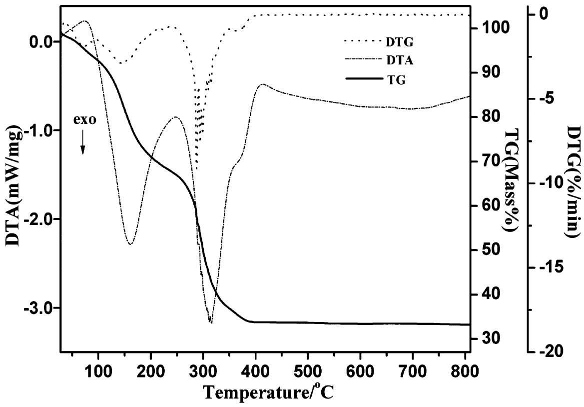

Fig. 3. TG–DTG–DTA plot of $Co_{0.4}Ni_{0.2}Zn_{0.4}Fe_2\ (C_4H_2O_4)_3{\cdot}6N_2H_4$.