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Synthesis and characterization of $Co_{0.8}Zn_{0.2}Fe_2O_4$ nanoparticles

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Abstract Cobalt zinc ferrite, $Co_{0.8}Zn_{0.2}Fe_2O_4$, nanoparticles have been synthesized via autocatalytic decomposition of the precursor, cobalt zinc ferrous fumarato hydrazinate. The X-ray powder diffraction of the 'as prepared' oxide confirms the formation of single phase nanocrystalline cobalt zinc ferrite nanoparticles. The thermal decomposition of the precursor has been studied by isothermal, thermogravimetric and differential thermal analysis. The precursor has also been characterized by FTIR, and chemical analysis and its chemical composition has been determined as $Co_{0.8}Zn_{0.2}Fe_2(C_4H_2O_4)_3{\cdot}6N_2H_4$. The Curie temperature of the 'as-prepared oxide' was determined by AC susceptibility measurements.

Keywords Nanoparticles · Thermal analysis · Autocatalytic decomposition · Fumarato-hydrazinate precursor · Ferrite

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Introduction

It is eminent that materials in the realm of nanometer scale show unexpected behaviour with respect to its physical and chemical properties. Since the study of the properties of a material preludes technological applications, the ongoing trend to research and explore this dominion is quite apparent. Over the years, many synthetic strategies have been developed to prepare nanomaterials [1–6] having diverse applications [7–12].

During the last few years, our research group has been involved in synthesizing nanomaterials from novel precursors which are hydrazine derivatives of metal carboxylates [13–22]. These metal hydrazine carboxylates are in general pyrophoric in nature and they decompose at low temperatures leading to ultrafine oxide having high surface area. Hydrazine being a fuel not only supports combustion but also lowers the decomposition temperature of the metal complexes [18, 19]. This report elucidates the thermal decomposition pattern of a new precursor, cobalt zinc ferrous fumarato-hydrazinate which decomposes autocatalytically to give nanosized $Co_{0.8}Zn_{0.2}Fe_2O_4$.

Experimental

Preparation of cobalt zinc ferrous fumarato-hydrazinate

The cobalt zinc ferrous fumarato-hydrazinate precursor was synthesized by employing the method first devised by our group [20]. A requisite quantity of sodium fumarate in aqueous medium was stirred with hydrazine hydrate, $N_2H_4{\cdot}H_2O$ (99–100%) in an inert atmosphere for 2 h. To this, a freshly prepared solution containing ferrous chloride mixed with zinc chloride and cobalt chloride in

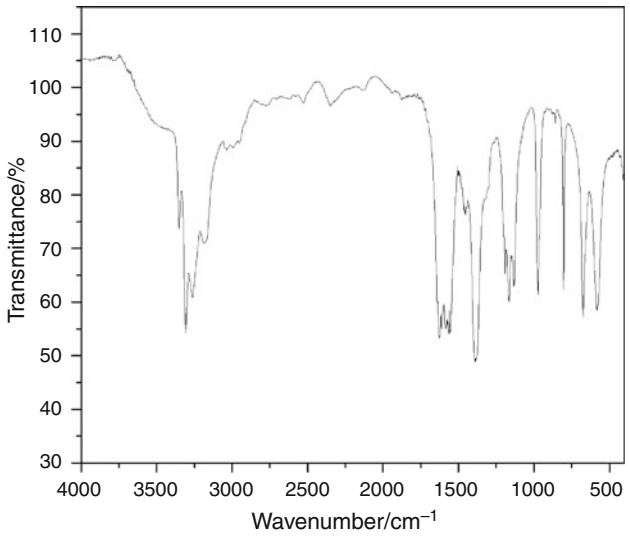

Fig. 1 Infrared spectra of $Co_{0.8}Zn_{0.2}(C_4H_2O_4)_3{\cdot}6N_2H_4$

stoichiometric amount was added drop-wise with constant stirring. The precipitate thus obtained was filtered off, washed with ethanol, dried with diethyl ether and stored in vacuum desiccators.

Methods of characterization

The precursor was chemically analyzed using titration, to determine its hydrazine content using KIO_3 as the titrant [23]. The percentage of cobalt, zinc and iron in the precursor was estimated by the standard methods given in the Vogel's textbook [23]. Infrared analysis of the precursor and its thermal products, i.e. $Co_{0.8}Zn_{0.2}Fe_2O_4$ was done on a Shimadzu FTIR—IR Prestige-21 spectrophotometer.

The thermal decomposition pattern of the precursor was studied by simultaneous differential thermal analysis (DTA) and thermogravimetric (TG) analysis on a NETZSCH, STA 409 PC (Luxx) analyzer from RT to 900 °C in dry air. The heating rate was maintained at 10 °C min^{-1}. The isothermal and total weight loss studies of the sample were also carried out at different predetermined temperatures. The Philips X-Ray diffractometer model PW 1710 with Cu Kα radiation and Ni filter was used to get the structural information of the decomposed product. The variation of AC susceptibility as a function of temperature [24] was used to find out the Curie temperature of the 'as-prepared oxide'.

Autocatalytic decomposition of the precursor

The dried precursor was spread on a Petri dish and ignited with a burning splinter. A small portion of it caught fire which spread immediately to the entire bulk. The precursor decomposes auto-catalytically in this manner, in an ordinary atmosphere to yield nanosized particles of the ferrite. This nanosized particle of the ferrite is termed as 'as-prepared oxide' in the text.

Results and discussion

Chemical formula determination of cobalt zinc ferrous fumarato-hydrazinate:

The infrared spectra of the complex (Fig. 1) shows three absorption bands in the region 3150–3300 cm^{-1} due to the N–H stretching frequencies. The N–N stretching frequencies at 972 cm^{-1} prove the bidentate bridging nature of the hydrazine ligand unequivocally. The asymmetric and symmetric stretching frequencies of the carboxylate ions are seen at 1596 and 1390 cm^{-1}, respectively with the Δv ($v_{asy} - v_{sym}$) separation of 206 cm^{-1}, which indicate the monodentate linkage of both carboxylate groups in the dianion. The IR data confirms the formation of cobalt zinc ferrous fumarato-hydrazinate complex.

The chemical formula, $Co_{0.8}Zn_{0.2}Fe_2(C_4H_2O_4)_3{\cdot}6N_2H_4$ has been assigned to the complex, cobalt zinc ferrous fumarato-hydrazinate based on the observed percentage of hydrazine (27.07), Cobalt (19.86), Zinc (5.55) and Iron (47.44) which match closely with the calculated values of 27.20, 19.98, 5.54 and 47.34% for hydrazine, cobalt, zinc and iron, respectively (Table 1). Similarly, the observed mass loss of 66.24% in total mass loss studies (~800 °C) matches with the calculated value 66.58% based on the above mentioned formula.

Thermal analysis of the precursor:

The TG–DSC trace of thermal decomposition of $Co_{0.8}Zn_{0.2}Fe_2(C_4H_2O_4)_3{\cdot}6N_2H_4$ is shown in Fig. 2. The TG curve, from room temperature to 900 °C shows three mass loss regions with two major ones (Table 2). The mass losses of 8.96 and 18.11% from RT to 90 °C and from 90 to 180 °C were due to the loss of two N_2H_4 and four N_2H_4

Table 1 Chemical analysis and total weight loss data of cobalt zinc ferrous fumarato-hydrazinate precursor, $Co_{0.8}Zn_{0.2}Fe_2(C_4H_2O_4)_3{\cdot}6N_2H_4$

Complex	Cobalt/%		Zinc/%		Iron/%		Hydrazine/%		Total weight loss/%	
	Obs.	Cal.	Obs.	Cal.	Obs.	Cal.	Obs.	Cal.	Obs.	Cal.
$Co_{0.8}Zn_{0.2}Fe_2(C_4H_2O_4)_3{\cdot}6N_2H_4$	19.86	19.98	5.55	5.543	47.44	47.34	27.07	27.20	66.60	66.58

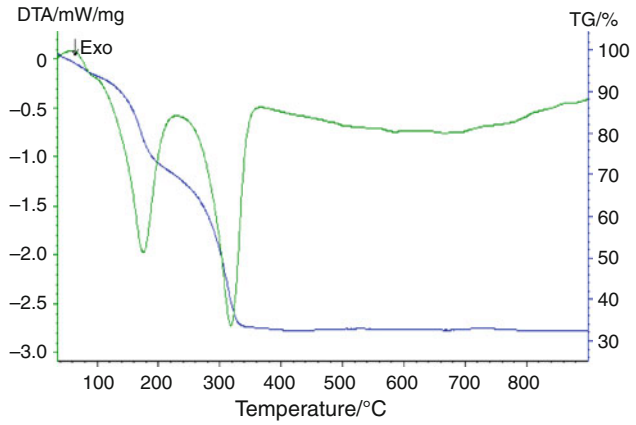

Fig. 2 TG–DSC curves of $Co_{0.8}Zn_{0.2}Fe_2(C_4H_2O_4)_3{\cdot}6N_2H_4$

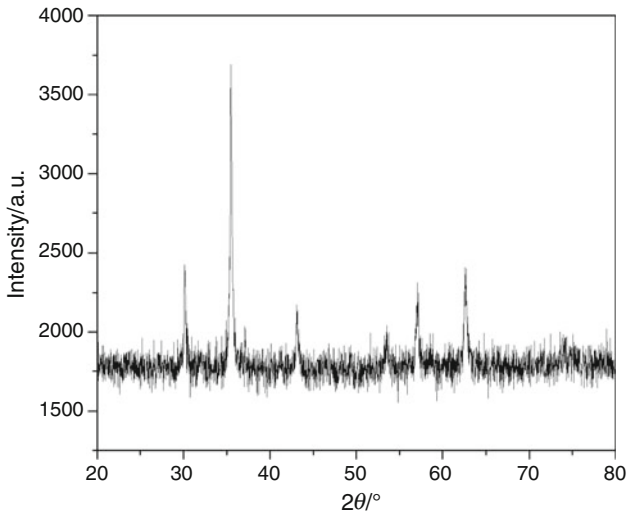

Fig. 3 XRD pattern of 'as prepared' $Co_{0.8}Zn_{0.2}O_4$

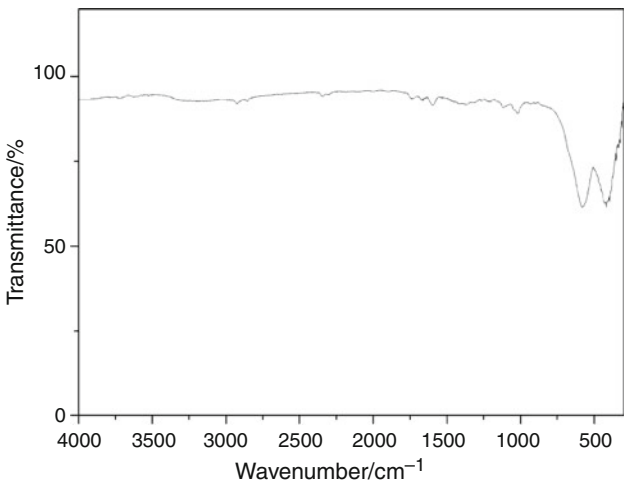

Fig. 4 Infrared spectra of 'as prepared' $Co_{0.8}Zn_{0.2}Fe_2O_4$

molecules, respectively. The DTA curve shows a small exothermic hump at 95 °C followed by another sharp exothermic peak at 174 °C due to dehydrazination as explained above. The major mass loss of 30.22% from 180 to 335 °C in the TG curve was due to decarboxylation of dehydrazinated fumarate precursor. DTA curve shows one sharp exothermic peak in this region with the peak temperature at 318 °C due to oxidative decarboxylation. A marginal mass loss of 3.81% was observed from 335 to 900 °C on the TG curve due to the oxidation of unburned carbon.

The weight loss studies of the precursor carried out separately at 400 °C shows total mass loss of 66.6%. It has been reported that the hydrazinated precursors loses the hydrazine molecules in presence of air between 100 and 300 °C [18]. It reacts explosively with atmospheric oxygen liberating enormous amount of energy which is sufficient to oxidatively decompose the hydrazinated complex into its respective metal oxide. The formation of monophasic $Co_{0.8}Zn_{0.2}Fe_2O_4$ nanoparticles soon after the autocatalytic thermal decomposition of the precursor has been confirmed by XRD (Fig. 3). The bands in the IR spectra of $Co_{0.8}Zn_{0.2}Fe_2O_4$ (Fig. 4) are in agreement with the reported ones [8]. The Curie temperature of the 'as-prepared oxide' determined by AC susceptibility measurements was found to be 369 °C which is on the lower side than that of bulk oxide sintered at 1200 °C [7] (Fig. 5). The lower value of T_c for 'as prepared' cobalt zinc ferrite is due to its nanosize particles and the similar observations has also been reported by other researchers in the literature [25, 26].

Table 2 TG–DTA data of cobalt zinc ferrous fumarato-hydrazinate precursor, $Co_{0.8}Zn_{0.2}Fe_2(C_4H_2O_4)_3{\cdot}6N_2H_4$

Complex	TG		DTA	Remarks
	Temp range/°C	Mass loss/%	Peak temp/°C	
$Co_{0.8}Zn_{0.2}Fe_2$ $(C_4H_2O_4)_3{\cdot}6N_2H_4$	RT–90	8.96	95.0 (exo hump)	Loss of two N_2H_4 molecule
	90–180	18.11	174.0 (exo)	Loss of four N_2H_4 molecule
	180–335	30.22	318.0 (exo)	Decarboxylation of dehydrazinated precursor
	335–900	3.81	–	

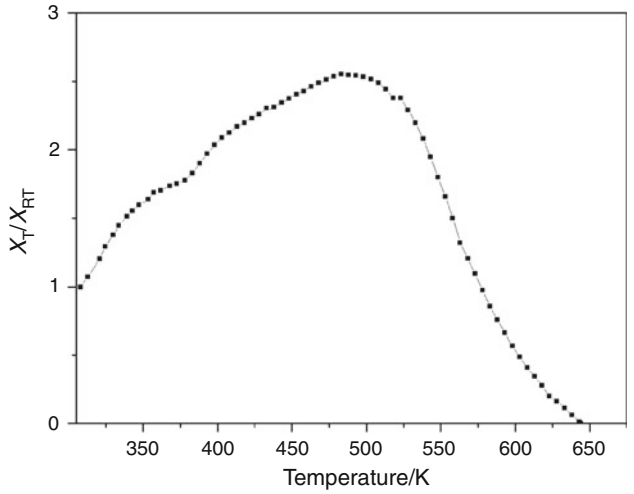

Fig. 5 AC susceptibility versus temperature plot of 'as prepared' $Co_{0.8}Zn_{0.2}Fe_2O_4$

Conclusions

The mixed metal fumarato-hydrazinate precursor offers a convenient synthetic route to prepare nanosized mixed metal oxides. In this study too, the hydrazine precursor exhibits autocatalytic decomposition behaviour after ignition in air, forming nanosize $Co_{0.8}Zn_{0.2}Fe_2O_4$. The chemical analysis, total mass loss and infrared spectral analysis of the complex confirms the formation of the complex with the formula $Co_{0.8}Zn_{0.2}Fe_2(C_4H_2O_4)_3{\cdot}6N_2H_4$. The TG–DSC studies of the complex show two step dehydrazination followed by two step decarboxylation to form single phase $Co_{0.8}Zn_{0.2}Fe_2O_4$ nanoparticles. The formation of $Co_{0.8}Zn_{0.2}Fe_2O_4$ was confirmed by XRD and IR. The Curie temperature of the 'as-prepared oxide' was found to be 369 °C which is far lower than expected indicating nanosize nature of particles.

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