

Synthesis and characterization of nanosize nickel-doped cobalt ferrite obtained by precursor combustion method

L. R. Gonsalves · V. M. S. Verenkar

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Abstract Nanoparticles of the spinel ferrite, $\text{Co}_{1-x}\text{Ni}_x\text{Fe}_2\text{O}_4$ ($x = 0, 0.2, 0.3$) have been synthesized by the precursor combustion technique. Novel precursors of metal fumarato-hydrazinate have been employed to yield the nanosized spinel ferrite. A characteristic feature of these precursors is that they decompose autocatalytically after ignition to give the monophasic nanocrystalline ferrite. This fact is corroborated by X-ray powder diffraction analysis. The thermal decomposition pattern of the precursors has been studied by isothermal thermogravimetric and differential thermal analysis. In order to fix the chemical composition, the precursors have been characterized by FTIR and chemical analysis and their chemical composition has been fixed accordingly. The Curie temperature of the “as-prepared” oxide was determined by alternating current susceptibility measurements.

Keywords Nanoparticles · Spinel ferrite · Magnetic properties · Autocatalytic decomposition · Thermal analysis · Fumarato-hydrazinate precursor

Introduction

Magnetic nanoparticles continue to evoke interest largely due to their prospective applicability. The spinel ferrite is a widely studied class of materials having remarkable magnetic and electric properties which have applications in high-density recording media, microwave devices, magnetic fluids, medical diagnostics, humidity sensors, etc.

[1–4]. Since understanding the structure and size-dependent properties is the key to tailor such materials, efforts are driven towards this goal. This has led to the development of many synthetic techniques which are being widely used for the synthesis of nanomaterials. Some of these include spray pyrolysis method, microemulsion synthesis, hydrothermal synthesis, reverse micelle technique, etc. [5–10].

This study deals with the synthesis of nickel-doped cobalt ferrite nanoparticles by employing the precursor combustion technique devised indigenously [11–16]. This technique makes use of novel precursors which are hydrazine derivatives of metal carboxylates. 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 [17]. The thermal reactivity of the metal–hydrazine complexes is also noteworthy as the stability of the complexes changes dramatically depending on the anion and cation [18]. This report demonstrates the thermal decomposition pattern of the cobalt nickel ferrous fumarato-hydrazinate precursors which decompose autocatalytically to give nanosized $\text{Co}_{1-x}\text{Ni}_x\text{Fe}_2\text{O}_4$.

Experimental

Preparation of cobalt nickel ferrous fumarato-hydrazinate

The cobalt nickel ferrous fumarato-hydrazinate precursors were synthesized by employing the method first devised and reported elsewhere [19]. A requisite quantity of sodium fumarate in aqueous medium was stirred with hydrazine hydrate, $\text{N}_2\text{H}_4 \cdot \text{H}_2\text{O}$ (99–100%) in an inert nitrogen

L. R. Gonsalves · V. M. S. Verenkar (✉)
Department of Chemistry, Goa University,
Taleigao Plateau, Goa 403206, India
e-mail: vmsv@rediffmail.com

atmosphere for 2 h. To this, a freshly prepared solution containing ferrous chloride mixed with nickel chloride and cobalt chloride in stoichiometric amount was added dropwise with constant stirring. The precipitate thus obtained was filtered, washed with ethanol, dried with diethyl ether and stored in a vacuum desiccator.

Methods of characterization

The precursors were chemically analysed by titrimetry, to determine the hydrazine content by using KIO_3 as the titrant [20]. The percentage of cobalt, nickel, and iron was also estimated by standard methods given in the Vogel's textbook [20]. Infrared analysis of the precursors and their thermal products, i.e., $\text{Co}_{1-x}\text{Ni}_x\text{Fe}_2\text{O}_4$ were done on Shimadzu FTIR Prestige-21 spectrophotometer.

The thermal decomposition pattern of the precursors 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 total weight loss studies of the samples were also carried out at a predetermined temperature.

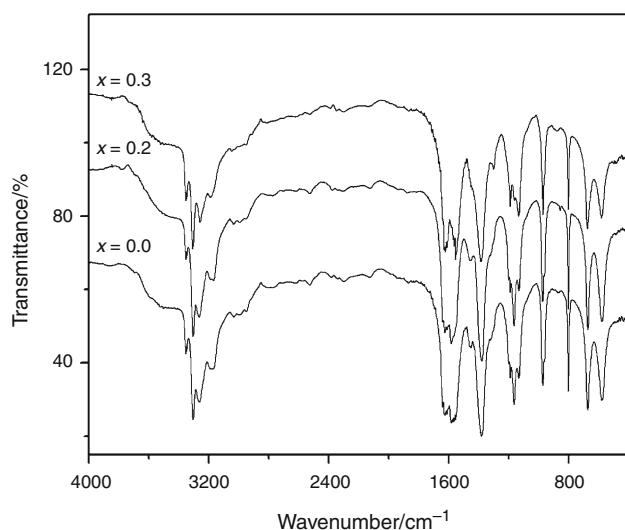


Fig. 1 Infrared spectra of the precursor $\text{Co}_{1-x}\text{Ni}_x(\text{C}_4\text{H}_2\text{O}_4)_3 \cdot 6\text{N}_2\text{H}_4$ ($x = 0, 0.2, 0.3$)

Table 1 Chemical analysis and total weight loss data of cobalt nickel ferrous fumarato-hydrazinate precursor, $\text{Co}_{1-x}\text{Ni}_x\text{Fe}_2(\text{C}_4\text{H}_2\text{O}_4)_3 \cdot 6\text{N}_2\text{H}_4$ ($x = 0, 0.2, 0.3$)

Complex	Cobalt%		Nickel%		Iron%		Hydrazine%		Total weight loss%	
	Obs.	Cal	Obs.	Cal	Obs.	Cal	Obs.	Cal	Obs.	Cal
$\text{CoFe}_2(\text{C}_4\text{H}_2\text{O}_4)_3 \cdot 6\text{N}_2\text{H}_4$	8.35	8.36	–	–	15.84	15.85	26.95	27.25	66.46	66.70
$\text{Co}_{0.8}\text{Ni}_{0.2}\text{Fe}_2(\text{C}_4\text{H}_2\text{O}_4)_3 \cdot 6\text{N}_2\text{H}_4$	6.63	6.69	1.6	1.7	15.84	15.85	27.03	27.25	66.58	66.70
$\text{Co}_{0.7}\text{Ni}_{0.3}\text{Fe}_2(\text{C}_4\text{H}_2\text{O}_4)_3 \cdot 6\text{N}_2\text{H}_4$	5.76	5.86	2.4	2.5	15.81	15.85	27.12	27.25	66.02	66.71

Autocatalytic decomposition of the precursor

The dried precursors were 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 precursors decompose autocatalytically in this manner, in an ordinary atmosphere to yield nanosize particles of the ferrite.

Results and discussion

Chemical formula determination of cobalt nickel ferrous fumarato-hydrazinate

The infrared spectra of all the complexes (Fig. 1) show three absorption bands in the region 3,185–3,350 cm^{-1} due to the N–H stretching frequencies. The N–N stretching frequencies at $\sim 974 \text{ cm}^{-1}$ proves the bidentate bridging nature of the hydrazine ligand [21]. The asymmetric and symmetric stretching frequencies of the carboxylate ions are seen at $\sim 1,585$ and $1,383 \text{ cm}^{-1}$, respectively, with the $\Delta\nu$ ($\nu_{\text{asy}} - \nu_{\text{sym}}$) separation of 202 cm^{-1} , which indicate the monodentate linkage of both carboxylate groups in the dianion. The IR data confirms the formation of cobalt nickel ferrous fumarato-hydrazinate in all of the complexes.

The chemical formula, $\text{Co}_{1-x}\text{Ni}_x\text{Fe}_2(\text{C}_4\text{H}_2\text{O}_4)_3 \cdot 6\text{N}_2\text{H}_4$ has been assigned to the complex, cobalt nickel ferrous fumarato-hydrazinate based on the observed percentage of hydrazine, cobalt, nickel, and iron which match closely with the calculated values (Table 1). Similarly, the observed mass loss in the total mass loss studies ($\sim 800 \text{ }^\circ\text{C}$) matches with the calculated value based on the above mentioned formula.

Thermal analysis of the precursor

The TG–DTA thermal decomposition patterns of $\text{Co}_{1-x}\text{Ni}_x\text{Fe}_2(\text{C}_4\text{H}_2\text{O}_4)_3 \cdot 6\text{N}_2\text{H}_4$ ($x = 0.0, 0.2, 0.3$) are shown in Fig. 2. The TG curve of all the complexes, from room temperature to 900 °C shows three mass loss regions with two major ones. The precursor with $x = 0$ shows a mass loss of 8.98 and 17.98% from RT to 98 °C and from 98 to 170 °C due to the loss of two and four N_2H_4 molecules,

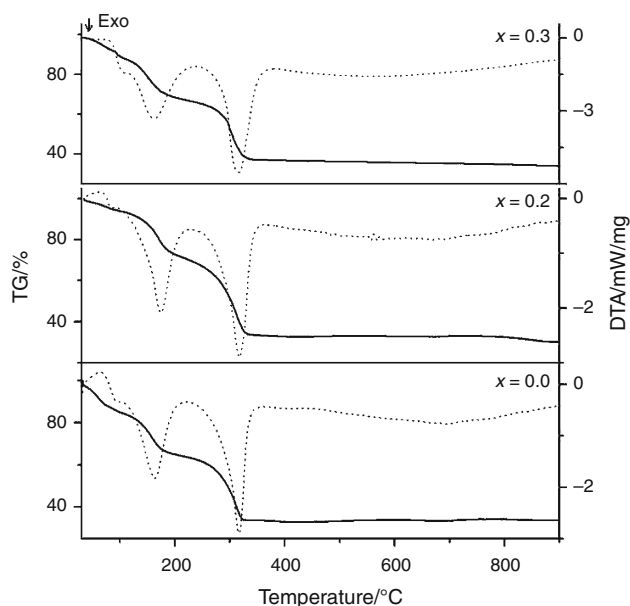


Fig. 2 TG-DSC curve of $\text{Co}_{1-x}\text{Ni}_x\text{Fe}_2(\text{C}_4\text{H}_2\text{O}_4)_3 \cdot 6\text{N}_2\text{H}_4$ ($x = 0, 0.2, 0.3$)

respectively. The DTA curve shows a small exothermic hump at 96.5 °C followed by a sharp exothermic peak at 162.8 °C due to dehydrazination, as explained. The major mass loss of 38.45% from 170 to 320 °C was due to decarboxylation of the dehydrazinated precursor. DTA curve shows one sharp peak in this region at 316.4 °C due to oxidative decarboxylation. A marginal mass loss of 0.34% was observed from 320 °C to 900 °C due to oxidation of unburned carbon.

The precursor with composition $x = 0.3$ decomposes with a similar three-step decomposition pattern, dehydrazination followed by decarboxylation. The TG shows mass losses of 9.05% from RT to 95 °C and 18.11% from 95 to 170 °C due to loss of two and four N_2H_4 molecules, respectively. Corresponding DTA peaks are observed at 93.2 °C (exothermic hump) and at 162.3 °C. The peak due to decarboxylation is observed at 318.7 °C and the TG shows a mass loss of 36.17% from 170 to 320 °C. A marginal mass loss of 3.27% is observed due to the unburned carbon from 320 to 900 °C. However, the precursor having the composition $x = 0.2$, although decomposes in a similar way, it loses one N_2H_4 molecule first at 85.5 °C followed by loss of five N_2H_4 molecules at 174.8 °C as seen in the DTA curve while the TG shows mass losses of 4.45% from RT to 90 °C and 22.7% from 90 to 175 °C due to dehydrazination. The major mass loss due to decarboxylation was found to be 35.26% from 175 to 320 °C a corresponding sharp exothermic peak at 317 °C is seen in the DTA curve. A marginal mass loss of 3.89% is also observed in the TG curve from 320 to 900 °C due to the unburned carbon.

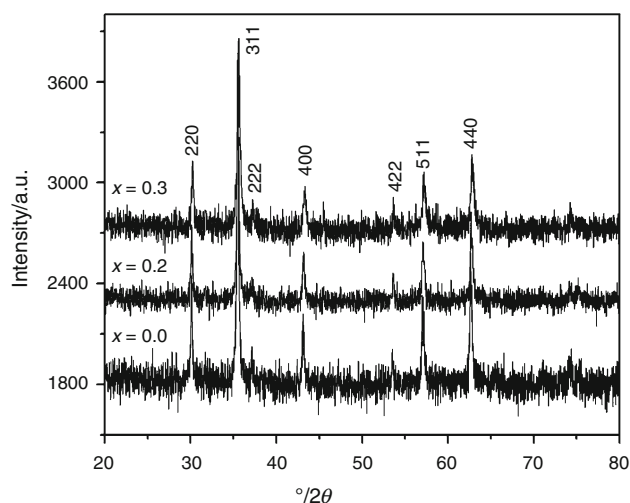


Fig. 3 XRD pattern of “as-prepared” $\text{Co}_{1-x}\text{Ni}_x\text{Fe}_2\text{O}_4$ ($x = 0, 0.2, 0.3$)

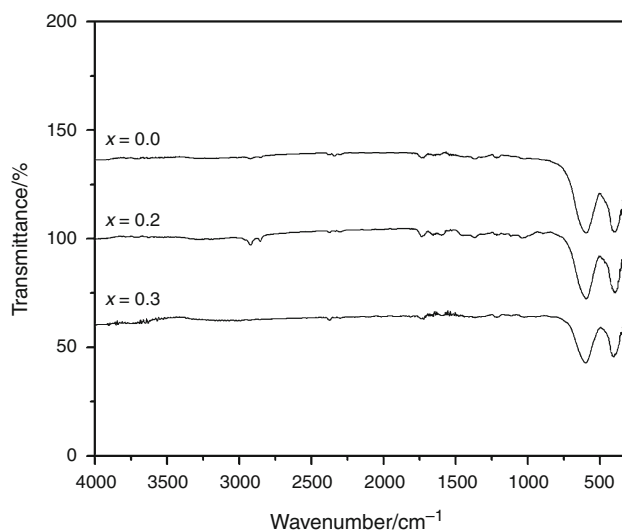


Fig. 4 Infrared spectra of “as-prepared” $\text{Co}_{1-x}\text{Ni}_x\text{Fe}_2\text{O}_4$ ($x = 0, 0.2, 0.3$)

The formation of monophasic $\text{Co}_{1-x}\text{Ni}_x\text{Fe}_2\text{O}_4$ nanoparticles soon after the autocatalytic thermal decomposition of the precursor has been confirmed by XRD (Fig. 3). The IR spectra (Fig. 4) of the “as-prepared” ferrites show high frequency ν_1 and low frequency ν_2 bands at around ~ 600 and 396 cm^{-1} , respectively. The ν_1 and ν_2 bands are assigned to the intrinsic vibration of the tetrahedral and octahedral groups. The Curie temperature, T_c , of the “as-prepared” oxide was determined using alternating current (ac) susceptibility measurements (Fig. 5). The Curie temperature was found to increase with the increase in nickel concentration. The T_c of cobalt ferrite ($x = 0.0$) was found to be 731 K, whereas the samples with $x = 0.2$ and 0.3 had a T_c of 743 and 747 K, respectively. The T_c values are comparable with the reported values [22].

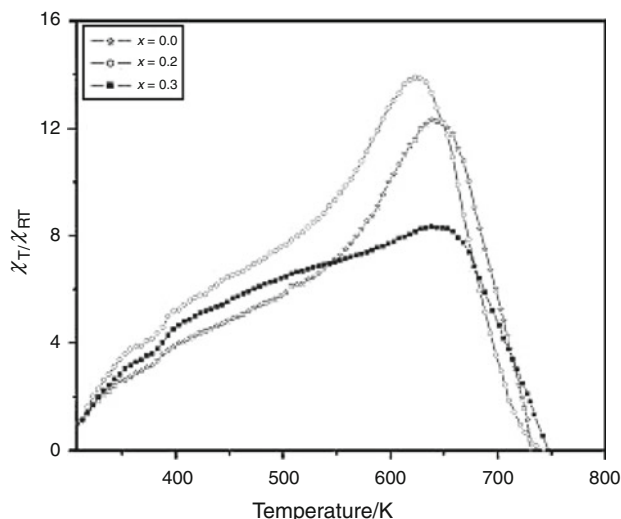


Fig. 5 AC susceptibility plot of “as-prepared” $\text{Co}_{1-x}\text{Ni}_x\text{Fe}_2\text{O}_4$ ($x = 0, 0.2, 0.3$)

Conclusions

The precursor combustion technique has been developed to produce uniform, ultrafine monophasic particles of the oxide. This synthetic strategy can be applied to synthesize different ferrites though the precursor may need to be chemically modified as per the desired end product. The precursor forms nanosize ferrite by way of autocatalytic decomposition after its ignition. The chemical analysis, total mass loss, and infrared spectral analysis of the complex confirms the formation of the complex and the formula $\text{Co}_{1-x}\text{Ni}_x\text{Fe}_2(\text{C}_4\text{H}_2\text{O}_4)_3 \cdot 6\text{N}_2\text{H}_4$ ($x = 0, 0.2, 0.3$) has been accordingly fixed. The TG–DSC studies of the complex show two-step dehydrazination followed by two-step decarboxylation to form single phase $\text{Co}_{1-x}\text{Ni}_x\text{Fe}_2\text{O}_4$ nanoparticles. This has been confirmed by XRD and IR. The Curie temperature of the samples was found to be comparable with the reported values.

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