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$Ni_{0.5}Mn_{0.1}Zn_{0.4}Fe_2(C_4H_2O_4)_3 \cdot 6N_2H_4$ PRECURSOR AND $Ni_{0.5}Mn_{0.1}Zn_{0.4}Fe_2O_4$ NANOPARTICLE

Preparation, IR spectral, XRD, SEM-EDS and thermal analysis

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Metal carboxylato-hydrazinates are very good precursors for the synthesis of metal as well as mixed metal oxides as these, most of the times decomposes to nanosized oxides with high surface area at comparatively lower temperatures. In the present study one such novel precursor has been prepared and characterized by XRD, IR, SEM-EDS and chemical analysis. The thermal decomposition of the precursor has also been studied by isothermal, differential scanning calorimetry (DSC) and thermogravimetric analysis (TG). The precursor shows two-step dehydrazination followed by decarboxylation to form $Ni_{0.5}Mn_{0.1}Zn_{0.4}Fe_2O_4$. The infrared spectra show N–N stretching frequency at 972 cm^{-1} which confirms the bidentate bridging hydrazine. XRD confirms the formation of single phase $Ni_{0.5}Mn_{0.1}Zn_{0.4}Fe_2O_4$.

Keywords: *autocatalytic decomposition, DSC, hydrazine precursor,* $Ni_{0.5}Mn_{0.1}Zn_{0.4}Fe_2O_4$ *nanoparticle, TG*

Introduction

The chemistry of hydrazine is of interest because it forms various complexes with transition metals whose stability changes dramatically, depending upon the anions as well as the cations [1–3]. Secondly, hydrazine being a fuel not only supports combustion but also lowers the decomposition temperature of the metal complexes. These complexes are important as precursors to obtain simple as well as ultrafine mixed metal oxides, which can have interesting electrical, magnetic and catalytic properties. Many researchers have studied organic-inorganic materials including hydrazine derivatives of metal carboxylates since they serve as precursors to fine particle oxide materials relatively at much lower temperatures and also characterized them using various techniques such DSC, DTA, TG, SEM, TEM, XRD, AAS and FTIR spectroscopy [4–41].

We are reporting here the preparation and characterization of nickel manganese zinc ferrous fumarato–hydrazinate precursor and its thermal decomposition to $Ni_{0.5}Mn_{0.1}Zn_{0.4}Fe_2O_4$ nanoparticles.

Experimental

Preparation and characterization

Preparation of nickel manganese zinc ferrous fumarato–hydrazinate

The method given below for the preparation of nickel manganese zinc ferrous fumarato–hydrazinate has been described in detail elsewhere [42, 43]. A requisite quantity of sodium fumarate in aqueous medium was stirred with hydrazine hydrate (99–100%) in an inert atmosphere for 2 h. To this solution, a stoichiometric amount of freshly prepared ferrous chloride solution mixed with manganese chloride, nickel chloride and zinc chloride was added dropwise with constant stirring in an inert atmosphere. The yellow colour precipitate thus obtained was filtered off, washed with ethanol, dried with diethyl ether and then stored in vacuum desiccators.

Characterization

The hydrazine content in the precursor was determined by volumetric analysis using standard 0.025 M KIO_3 solution under Andrew's conditions [44]. The metal contents were determined using chemical analysis and SEM-EDS analysis using scanning electron microscope model JEOL 5800LV.

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The structure and phase purity of the nickel manganese zinc ferrite (as prepared) was determined by Rigaku X-ray diffractometer model D Max II C using CuKα radiations and Ni filter. Simultaneous thermogravimetric and differential scanning calorimetry of precursor and 'as prepared' nickel manganese zinc ferrite was recorded on Netzsch DSC-TG STA 409PC at a heating rate of 10°C min^{-1}. The isothermal and total mass loss studies of the precursor were carried out along with hydrazine estimation at various predetermined temperatures. Infrared analysis of the precursor and $Ni_{0.5}Mn_{0.1}Zn_{0.4}Fe_2O_4$ was done on a FTIR Shimadzu IR prestige 21 series spectrophotometer.

Autocatalytic decomposition of the complex

These precursors once ignited, decompose autocatalytically to form $Ni_{0.5}Mn_{0.1}Zn_{0.4}Fe_2O_4$ at lower temperature. For this autocatalytic decomposition, the precursor was first spread over a Petri dish and a burning splinter was brought near to it, when small portion of it caught fire. A red glow that subsequently formed spread over the entire bulk completing the total decomposition of the precursor in an ordinary atmosphere to form nickel manganese zinc ferrite nanoparticle powder.

Results and discussion

Chemical formula fixation of nickel manganese zinc ferrous fumarato–hydrazinate

A chemical formula of $Ni_{0.5}Mn_{0.1}Zn_{0.4}Fe_2(C_4H_2O_4)_3\cdot 6N_2H_4$ for nickel manganese zinc ferrous fumarato–hydrazinate precursor has been fixed based on the total percentage mass loss of 66.63 and percentages of hydrazine 27.44, nickel 4.12, manganese 0.784, zinc 3.67 and iron 15.93 which match closely with the calculated value of 66.53, 27.19, 4.15, 0.777, 3.70 and 15.81 for total percentage mass loss, percentages of hydrazine, nickel, manganese, zinc and iron, respectively (Table 1). The infrared spectra of the precursor (Fig. 1) showed three bands in the region 3259–3352 cm^{-1} due to the N–H stretching frequencies and in the range of 1552–1583 cm^{-1} due to NH_2 deformation. The N–N stretching frequency was observed at 972 cm^{-1} which confirmed the bidentate bridging nature of hydrazine ligand [45]. The asymmetric and symmetric stretching frequencies of the carboxylate ion in the precursor are seen at 1627 and 1390 cm^{1}, respectively with $\Delta\nu$ ($\nu_{\text{asym}}-\nu_{\text{sym}}$) separation of 237 cm^{-1} indicating the monodentate linkage of both carboxylate groups in the dianions [45, 46]. Thus, the fumarate dianions in the complex coordinate to the metal as bidentate ligand via both the carboxylate groups. These results suggest the formation of nickel manganese zinc ferrous fumarato–hydrazinate complex.

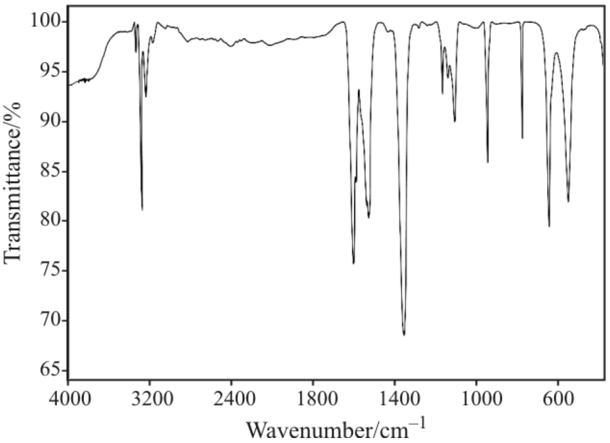

Fig. 1 Infrared spectra of nickel manganese zinc ferrous fumarato–hydrazinate

Thermal analysis of the complex and phase identification of the product

Nickel manganese zinc ferrous fumarato–hydrazinate precursor was decomposes in air, thermally and autocatalytically to $Ni_{0.5}Mn_{0.1}Zn_{0.4}Fe_2O_4$.

The '*d*' values calculated from the X-ray diffraction pattern of the autocatalytically decomposed end product of the complex confirm formation of spinel structure.

TG, DSC, isothermal mass loss and hydrazine analysis

The TG curves (Fig. 2) of $Ni_{0.5}Mn_{0.1}Zn_{0.4}Fe_2(C_4H_2O_4)_3.6N_2H_4$ in air from room temperature to 800°C shows four mass loss regions with two major ones. The mass loss of 4.59 and 22.62% from room temperature to 130 and from 130 to 155°C were due to the loss of one hydrazine and five hydrazine molecules, respectively

Table 1 Chemical and thermal analysis of nickel manganese zinc ferrous fumarato–hydrazinate $Ni_{0.5}Mn_{0.1}Zn_{0.4}Fe_2(C_4H_2O_4)_3\cdot 6N_2H_4$

Complex	Nickel/		Manganese/		Zinc/		Iron/		Hydrazine/		Total mass loss/	
	%											
$Ni_{0.5}Mn_{0.1}Zn_{0.4}Fe_2$ $(C_4H_2O_4)_3\cdot 6N_2H_4$	obs.	calc.	obs.	calc.	obs.	calc.	obs.	calc.	obs.	calc.	obs.	calc.
	4.12	4.15	0.784	0.777	3.67	3.70	15.93	15.81	27.44	27.19	66.63	66.53

Table 2 TG-DSC, isothermal mass loss and hydrazine analysis data of nickel manganese zinc ferrous fumarato–hydrazinate, $Ni_{0.5}Mn_{0.1}Zn_{0.4}Fe_2(C_4H_2O_4)_3\cdot 6N_2H_4$

Complex	TG		DSC	Remarks	Isothermal mass loss/hydrazine analysis		
	temp. range/°C	mass loss/%	peak temp./°C (Effect)		temp. range/°C	mass loss/%	N_2H_4/%
$Ni_{0.5}Mn_{0.1}Zn_{0.4}Fe_2$ $(C_4H_2O_4)_3\cdot 6N_2H_4$	RT–130	4.59	87.7 (exo)	Loss of one N_2H_4 molecule	rT rT–130	0.00 4.59	27.44 23.87
	130–155	22.62	152.2 (exo)	Loss of five N_2H_4 molecule	130–151	55.44	Compound catches fire
	155–230	10.91	184.7 (exo)	Multistep decarboxylation of dehydrazinated precursor			
	230–340	21.17	317.5 (exo)				
	340–420	4.51	340–420 (broad exo hump)				

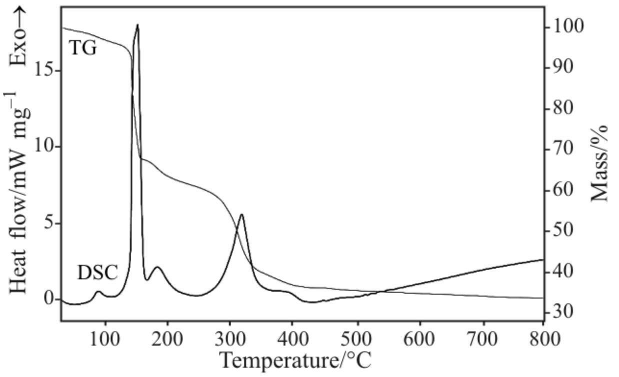

Fig. 2 TG-DSC curves of nickel manganese zinc ferrous fumarato–hydrazinate

(Table 2). DSC shows two sharp exotherms with a peak temperature of 87.7 and 152.2°C due to two-step dehydrazination. The mass loss of 10.91 and 21.17% in TG from 155 to 230 and 230 to 340°C, respectively can be attributed to the decarboxylation of the dehydrazinated precursor. DSC shows two exothermic peaks in this region with the peak temperature of 184.7 and 317.5°C due to two step oxidative decarboxylation. A marginal mass loss of 4.51% in the region 340 to 420°C may be due to unburned carbon which is indicated in the DSC by a broad exotherm in this region.

An isothermal mass loss study in air done on the precursor also confirms the loss of one hydrazine molecule up to 130°C. But this oxidative dehydrazination of single hydrazine molecule initiates the combustion of the entire precursor. Thus, the precursor catches fire at 151°C thereby undergoing simultaneous dehydrazination followed by decarboxylation in air, oxidatively.

The TG-DSC trace of 'as prepared' oxide does not show any change in the region from 250 to 550°C indicating the absence of any magnetic metastable oxides such as γ-Fe_2O_3 and Fe_3O_4 as an impurity which otherwise very difficult to detect in the X-ray diffraction analysis due to their similarity in structure with $Ni_{0.5}Mn_{0.1}Zn_{0.4}Fe_2O_4$.

Conclusions

- Nickel manganese zinc ferrous fumarato–hydrazinate can be synthesized easily from sodium fumarate, nickel chloride, manganese chloride, zinc chloride, ferrous chloride and hydrazine hydrate in an inert atmosphere at room temperature.
- Chemical analysis, EDS analysis, total mass loss and infrared studies of the complex confirms the formation of the complex with formula $Ni_{0.5}Mn_{0.1}Zn_{0.4}Fe_2(C_4H_2O_4)_3\cdot 6N_2H_4$.
- The precursor decomposes autocatalytically once ignited in air to form $Ni_{0.5}Mn_{0.1}Zn_{0.4}Fe_2O_4$.
- TG-DSC studies of the complex show two-step dehydrazination followed by decarboxylation to form $Ni_{0.5}Mn_{0.1}Zn_{0.4}Fe_2O_4$. TG-DSC of 'as prepared' $Ni_{0.5}Mn_{0.1}Zn_{0.4}Fe_2O_4$ shows no indication of presence of γ-Fe_2O_3 or Fe_3O_4 as impurity.
- XRD confirms the formation of the single phase $Ni_{0.5}Mn_{0.1}Zn_{0.4}Fe_2O_4$.

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