J Therm Anal Calorim (2012) 108:859–863
DOI 10.1007/s10973-012-2392-5

Synthesis and characterization of ultrafine spinel ferrite obtained by precursor combustion technique

L. R. Gonsalves · S. C. Mojumdar · V. M. S. Verenkar

CTAS2011 Conference Special Chapter

Abstract Nanoparticles of the spinel ferrite, $Co_{0.6}Ni_{0.4}Fe_2O_4$ have been synthesized by the precursor combustion technique. This synthetic route makes use of a novel precursor viz. metal fumarato hydrazinate which decomposes autocatalytically after ignition to yield nanosized spinel ferrite. The X-ray powder diffraction of the "as prepared" oxide confirms the formation of monophasic nanocrystalline cobalt nickel ferrite. 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 fixed as $Co_{0.6}Ni_{0.4}Fe_2(C_4H_2O_4)_3 \cdot 6N_2H_4$. The Curie temperature of the "as prepared" oxide was determined by ac susceptibility measurements.

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

L. R. Gonsalves · V. M. S. Verenkar
Department of Chemistry, Goa University, Taleigao Plateau, Goa 403206, India

S. C. Mojumdar (✉)
Department of Chemistry, University of Guelph, Guelph, ON, Canada
e-mail: scmojumdar@yahoo.com

S. C. Mojumdar
Department of Chemical Technologies and Environment, Faculty of Industrial Technologies, Trencin University of A. Dubceck, Puchov, Slovakia

Introduction

Magnetic nanoparticles of spinel ferrites are of great importance not only for its application potential but also for fundamental research [1–4]. Understanding the structure and size dependent properties is the key to the tailoring of materials with desired properties. In general, most of the material properties are sensitive to the preparation conditions and heat treatment and getting the material in the desired form and shape is quite a challenge. Material chemists have addressed this issue by developing new synthetic strategies and improving the existing ones to suit their requirements. Besides the existing age old methods like co-precipitation, precursor, sol–gel, new ones have also evolved for synthesizing nanoparticles. Some of these include spray pyrolysis method, microemulsion synthesis, hydrothermal synthesis, reverse micelle technique, etc. [5–10].

In the present study, we have successfully synthesized nanoparticles of spinel ferrite by employing the precursor combustion technique first devised by our group [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, 18]. Thermal and spectral analyses are very useful methods for materials characterization. Therefore, many authors have used these techniques for various materials characterization [13, 19–38].

This report demonstrates the thermal decomposition pattern of the precursor, cobalt nickel ferrous fumarato-hydrazinate which decomposes autocatalytically to give nanosized $Co_{0.6}Ni_{0.4}Fe_2O_4$.

Experimental

Preparation of cobalt nickel ferrous fumarato-hydrazinate

The cobalt nickel ferrous fumarato-hydrazinate precursor was synthesized by employing the method first devised by our group [39]. 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 and then 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 vacuum desiccators.

Characterization methods

The precursor was chemically analyzed by titration to determine its hydrazine content using KIO_3 as the titrant [40]. The percentage of cobalt, nickel, and iron was also estimated by standard methods given in the Vogel's textbook [40]. Infrared analysis of the precursor and its thermal products, i.e., $Co_{0.6}Ni_{0.4}Fe_2O_4$ was done on 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.

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 autocatalytically in this manner, in an ordinary atmosphere to yield ultrafine particles of the ferrite.

Results and discussion

Chemical formula determination of cobalt nickel ferrous fumarato-hydrazinate

The infrared spectra of the complex (Fig. 1) shows three absorption bands in the region 3,180–3,355 cm^{-1} due to the N–H stretching frequencies. The N–N stretching frequencies at 972 cm^{-1} clearly proves the bidentate bridging nature of the hydrazine ligand [41]. The asymmetric and symmetric stretching frequencies of the carboxylate ions are seen at 1,587 and 1,379 cm^{-1}, respectively with the Δv ($v_{asy} - v_{sym}$) separation of 208 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 complex.

The chemical formula, $Co_{0.6}Ni_{0.4}Fe_2(C_4H_2O_4)_3{\cdot}6N_2H_4$ has been assigned to the complex, cobalt nickel ferrous fumarato-hydrazinate based on the observed percentage of hydrazine (27.22), Cobalt (4.98), Nickel (3.29), and Iron (15.71) which match closely with the calculated values of 27.25, 5.02, 3.33, and 15.85 % for hydrazine, cobalt, nickel, and iron, respectively (Table 1). Similarly, the observed mass loss of 66.67 % in total mass loss studies (~800 °C) matches with the calculated value 66.71 % based on the above mentioned formula.

Thermal analysis of the precursor

The TG–DTA curves of $Co_{0.6}Ni_{0.4}Fe_2(C_4H_2O_4)_3{\cdot}6N_2H_4$ 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 9.11 and 18.12 % from RT to 95 °C and from 95 to 180 °C were due to the loss of two N_2H_4 and four N_2H_4 molecules, respectively. The DTA curve shows a small exothermic hump at 92.8 °C followed by another sharp exothermic peak at 159.3 °C due to dehydrazination as explained above. The major mass loss of 30.12 % from 180 to 310 °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 303.5 °C due to oxidative decarboxylation. A marginal mass loss of 3.21 % was

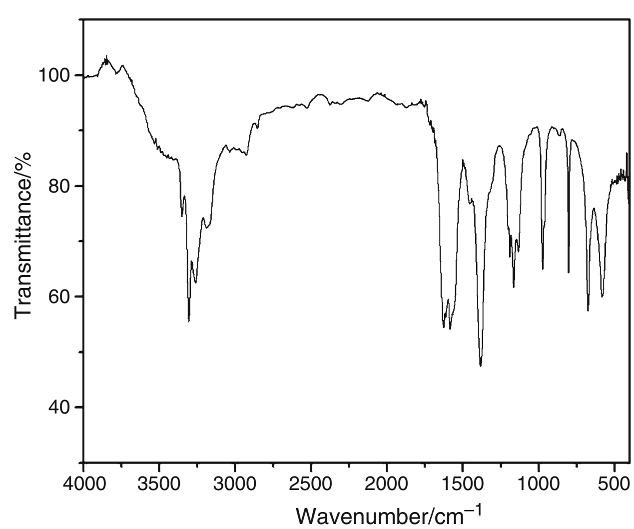

Fig. 1 Infrared spectra of $Co_{0.6}Ni_{0.4}(C_4H_2O_4)_3{\cdot}6N_2H_4$

Table 1 Chemical analysis and total mass loss data of cobalt nickel ferrous fumarato-hydrazinate precursor, $Co_{0.6}Ni_{0.4}Fe_2(C_4H_2O_4)_3{\cdot}6N_2H_4$

Complex	Cobalt/%		Nickel/%		Iron/%		Hydrazine/%		Total mass loss/%	
	Obs.	Cal.	Obs.	Cal.	Obs.	Cal.	Obs.	Cal.	Obs.	Cal.
$Co_{0.6}Ni_{0.4}Fe_2(C_4H_2O_4)_3{\cdot}6N_2H_4$	4.98	5.02	3.29	3.33	15.71	15.75	27.22	27.25	66.67	66.71

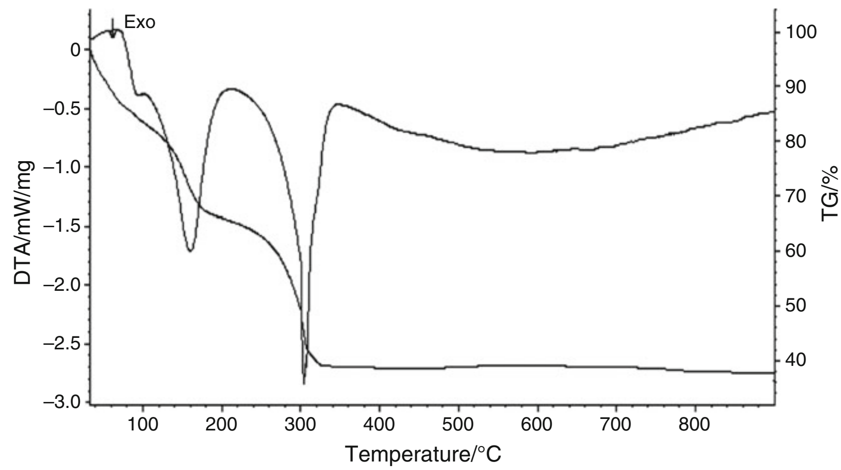

Fig. 2 TG–DTA curves of $Co_{0.6}Ni_{0.4}Fe_2(C_4H_2O_4)_3{\cdot}6N_2H_4$

Table 2 TG–DTA data of cobalt nickel ferrous fumarato-hydrazinate precursor, $Co_{0.6}Ni_{0.4}Fe_2(C_4H_2O_4)_3.6N_2H_4$

Complex	TG		DTA	Remarks
	Temp range/°C	Mass loss/%	Peak temp./°C	
$Co_{0.6}Ni_{0.4}Fe_2$ $(C_4H_2O_4)_3{\cdot}6N_2H_4$	RT-95	9.11	92.8 (exo hump)	Loss of two N_2H_4 molecule
	95–180	18.12	159.3 (exo)	Loss of four N_2H_4 molecule
	180–310	30.12	303.5 (exo)	Decarboxylation of dehydrazinated precursor
	310–900	3.06	–	

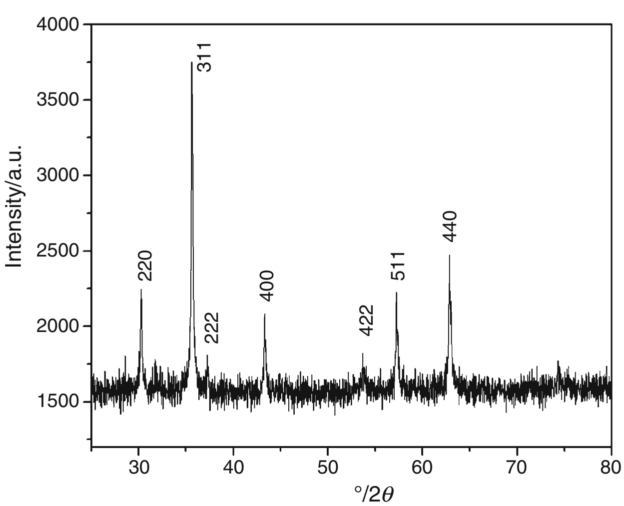

Fig. 3 XRD pattern of $Co_{0.6}Ni_{0.4}(C_4H_2O_4)_3{\cdot}6N_2H_4$

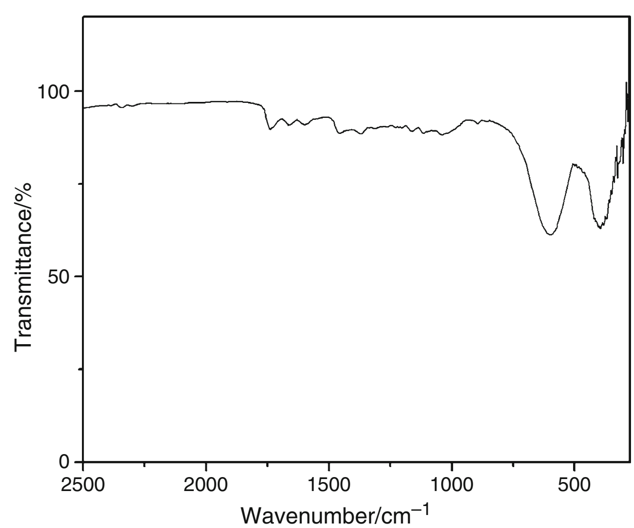

Fig. 4 Infrared spectra of 'as prepared' $Co_{0.6}Ni_{0.4}Fe_2O_4$

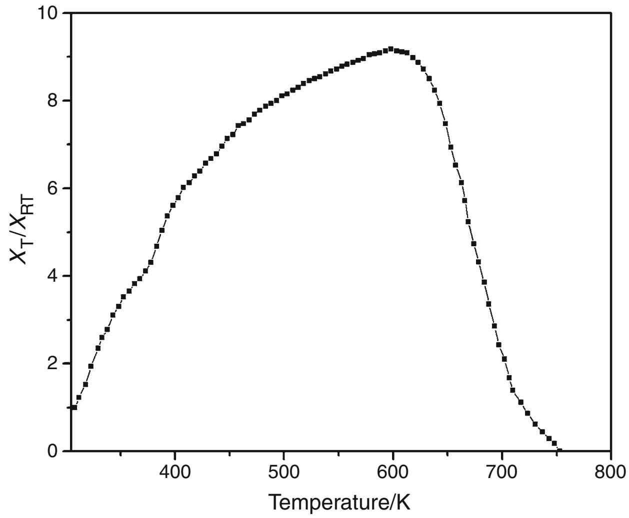

Fig. 5 a.c. susceptibility plot of 'as prepared' $Co_{0.6}Ni_{0.4}Fe_2O_4$

observed from 310 to 900 °C on the TG curve due to the oxidation of unburned carbon.

The mass loss studies of the precursor carried out separately at 400 °C shows total mass loss of 66.67 %. It has been reported that the hydrazinated precursors loses the hydrazine molecules in the presence of air between 100 and 300 °C [39]. 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 $Co_{0.6}Ni_{0.4}Fe_2O_4$ nanoparticles soon after the autocatalytic thermal decomposition of the precursor has been confirmed by XRD (Fig. 3). The IR spectra (Fig. 4) of the ferrite show high frequency v_1 and low frequency v_2 bands at around 599 and 398 cm^{-1}, respectively. The v_1 and v_2 bands are assigned to the intrinsic vibration of the tetrahedral and octahedral groups. The Curie temperature of the cobalt nickel ferrite was determined by a.c. susceptibility measurements and it was found to be 753 K (Fig. 5).

Conclusions

The precursor combustion technique via formation of mixed metal fumarato-hydrazinate precursor can be successfully employed to prepare nanosized spinel ferrites. The precursor forms nanosize $Co_{0.6}Ni_{0.4}Fe_2O_4$ 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 with the formula $Co_{0.6}Ni_{0.4}Fe_2(C_4H_2O_4)_3{\cdot}6N_2H_4$. The TG–DTA studies of the complex show two step dehydrazination followed by two step decarboxylation to form single phase $Co_{0.6}Ni_{0.4}Fe_2O_4$ nanoparticles. The formation of $Co_{0.6}Ni_{0.4}Fe_2O_4$ was confirmed by XRD and IR. The Curie temperature of the "as prepared" oxide was found to be 753 K.

References

1. Gedam NN, Padole PR, Rithe SK, Chaudhari GN. Ammonia gas sensor based on a spinel semiconductor, $Co_{0.8}Ni_{0.2}Fe_2O_4$ nanomaterial. J Sol-Gel Sci Technol. 2009;50:296–300.
2. Kamble RC, Shaikh PA, Kamble SS, Kolekar YD. Effect of cobalt substitution on structural, magnetic and electric properties of nickel ferrite. J Alloys Compd. 2009;478:599–603.
3. Sedlar M, Pust L. Preparation of cobalt doped nickel ferrite thin films on optical fibres by dip-coating technique. Ceram Int. 1995;21:21–7.
4. Chen Z, Gao L. Synthesis and magnetic properties of $CoFe_2O_4$ nanoparticles by using PEG as surfactant additive. Mater Sci Eng B. 2007;141:82–6.
5. Vital A, Angermann A, Dittmann R, Graule T, Topfer J. Highly sinter-active (Mg–Cu)–Zn ferrite nanoparticles prepared by flame spray synthesis. Acta Mater. 2007;55:1955–64.
6. Hua ZH, Chen RS, Li CL, Yang SG, Lu M, Gu XB, Du YW. $CoFe_2O_4$ nanowire arrays prepared by template-electrodeposition method and further oxidization. J Alloys Compd. 2007;427:199–203.
7. Thakur S, Katyal SC, Singh M. Structural and magnetic properties of nano nickel–zinc ferrite synthesized by reverse micelle technique. J Magn Magn Mater. 2009;321:1–7.
8. Maensiri S, Masingboon C, Boonchom B, Seraphin S. A simple route to synthesize nickel ferrite ($NiFe_2O_4$) nanoparticles using egg white. Scr Mater. 2007;56(9):797–800.
9. Jiang J. A facile method to the $Ni_{0.8}Co_{0.2}Fe_2O_4$ nanocrystalline via a refluxing route in ethylene glycol. Mater Lett. 2007;61: 3239–42.
10. Singhal S, Singh J, Barthwal SK, Chandra K. Preparation and characterization of nanosize nickel-substituted cobalt ferrites ($Co_{1-x}Ni_xFe_2O_4$). J Solid State Chem. 2005;178:3183–9.
11. Verenkar VMS, Rane KS. Thermal and electrothermal analysis (ETA) of iron(II) carboxylato-hydrazinates. Part I–Ferrous fumarato-hydrazinate and ferrous succinato-hydrazinate. In: Dharwadkar SR, Bharadwaj SR, Mukherjee SK, Sood DD, editors. Proceedings of the 10th national symposium on thermal analysis, Thermans. Kanpur: Indian Thermal Analysis Society; 1995. p. 171–4.
12. Verenkar VMS, Rane KS. Synthesis, characterization and thermal analysis of ferrous malato-hydrazinate. In: Ravindran PV, Sudersanan M, Misra NL, Venugopal V, editors. Proceedings of the 12th national symposium on thermal analysis, Thermans. Gorakhpur: Indian Thermal Analysis Society; 2000. p. 194–7.
13. Sawant SY, Verenkar VMS, Mojumdar SC. Preparation, thermal, XRD, chemical and FTIR spectral analysis of $NiMn_2O_4$ nanoparticles and respective precursor. J Therm Anal Calorim. 2007; 90:669–72.
14. More A, Verenkar VMS, Mojumdar SC. Nickel ferrite nanoparticles synthesis from novel fumarato-hydrazinate precursor. J Therm Anal Calorim. 2008;94(1):63–7.
15. Gonsalves LR, Verenkar VMS, Mojumdar SC. Preparation and characterization of $Co_{0.5}Zn_{0.5}Fe_2(C_4H_2O_4)_3{\cdot}6N_2H_4$: a precursor to prepare $Co_{0.5}Zn_{0.5}Fe_2O_4$ nanoparticles. J Therm Anal Calorim. 2009;96(1):53–7.
16. Gonsalves LR, Verenkar VMS, Mojumdar SC. Synthesis of cobalt nickel ferrite nanoparticles via autocatalytic decomposition of the precursor. J Therm Anal Calorim. 2010;100:789–92.

17. Porob RA, Khan SZ, Mojumdar SC, Verenkar VMS. Synthesis, TG, DSC and infrared spectral study of $NiMn_2(C_4H_4O_4)_3 \cdot 6N_2H_4$: a precursor for $NiMn_2O_4$ nano-particles. J Therm Anal Calorim. 2006;86(3):605–8.
18. More A, Mojumdar SC, Parab S, Verenkar VMS. Preparation, purification and characterization of nanoparticle ferrite from novel fumarato-hydrazinate precursor. In: 15th CTAS annual workshop and exhibition, May 17–18, National Research Council Canada, Bouchervile; 2005. p. 22.
19. Mojumdar SC, Raki L. Preparation, thermal, spectral and microscopic studies of calcium silicate hydrate-poly(acrylic acid) nanocomposite materials. J Therm Anal Calorim. 2006;85:99–105.
20. Porob RA, Khan SZ, Mojumdar SC, Verenkar VMS. Synthesis, TG, SDC and infrared spectral study of $NiMn_2(C_4H_4O_4)_3 \cdot 6N_2H_4$: a precursor for $NiMn_2O_4$ nanoparticles. J Therm Anal Calorim. 2006;86:605–8.
21. Mojumdar SC, Varshney KG, Agrawal A. Hybrid fibrous ion exchange materials: past, present and future. Res J Chem Environ. 2006;10:89–103.
22. Doval M, Palou M, Mojumdar SC. Hydration behaviour of C_2S and C_2AS nanomaterials, synthesized by sol–gel method. J Therm Anal Calorim. 2006;86:595–9.
23. Mojumdar SC, Moresoli C, Simon LC, Legge RL. Edible wheat gluten (WG) protein films: preparation, thermal, mechanical and spectral properties. J Therm Anal Calorim. 2011;104:929–36.
24. Varshney G, Agrawal A, Mojumdar SC. Pyridine based cerium(IV) phosphate hybrid fibrous ion exchanger: synthesis, characterization and thermal behaviour. J Therm Anal Calorim. 2007;90:731–4.
25. Mojumdar SC, Melnik M, Jona E. Thermal and spectral properties of Mg(II) and Cu(II) complexes with heterocyclic N-donor ligands. J Anal Appl Pyrolysis. 2000;53:149–60.
26. Mošner P, Vosejpková K, Koudelka L, Beneš L. Thermal studies of $ZnO–B_2O_3–P_2O_5–TeO_2$ glasses. J Therm Anal Calorim. 2012;107:1129–35.
27. Mojumdar SC, Sain M, Prasad RC, Sun L, Venart JES. Selected thermoanalytical methods and their applications from medicine to construction. J Therm Anal Calorim. 2007;60:653–62.
28. Meenakshisundarm SP, Parthiban S, Madhurambal G, Mojumdar SC. Effect of chelating agent (1,10-phenanthroline) on potassium hydrogen phthalate crystals. J Therm Anal Calorim. 2008;94:21–5.
29. Rejitha KS, Mathew S. Investigations on the thermal behavior of hexaamminenickel(II) sulphate using TG-MS and TR-XRD. Glob J Anal Chem. 2010;1(1):100–8.
30. Pajtášová M, Ondrušová D, Jóna E, Mojumdar SC, L'alíková S, Bazyláková T, Gregor M. Spectral and thermal characteristics of copper(II) carboxylates with fatty acid chains and their benzothiazole adducts. J Therm Anal Calorim. 2010;100:769–77.
31. Madhurambal G, Ramasamy P, Anbusrinivasan P, Vasudevan G, Kavitha S, Mojumdar SC. Growth and characterization studies of 2-bromo-4′-chloro-acetophenone (BCAP) crystals. J Therm Anal Calorim. 2008;94:59–62.
32. Gonsalves LR, Mojumdar SC, Verenkar VMS. Synthesis and characterisation of $Co_{0.8}Zn_{0.2}Fe_2O_4$ nanoparticles. J Therm Anal Calorim. 2011;104:869–73.
33. Raileanu M, Todan L, Crisan M, Braileanu A, Rusu A, Bradu C, Carpov A, Zaharescu M. Sol–gel materials with pesticide delivery properties. J Environ Protect. 2010;1:302–13.
34. Varshney KG, Agrawal A, Mojumdar SC. Pectin based cerium(IV) and thorium(IV) phosphates as novel hybrid fibrous ion exchangers synthesis, characterization and thermal behaviour. J Therm Anal Calorim. 2005;81:183–9.
35. Mojumdar SC, Šimon P, Krutošíková A. [1]Benzofuro[3,2-c]pyridine: synthesis and coordination reactions. J Therm Anal Calorim. 2009;96:103–9.
36. Moricová K, Jóna E, Plško A, Mojumdar SC. Thermal stability of $Li_2O–SiO_2–TiO_2$ gels evaluated by the induction period of crystallization. J Therm Anal Calorim. 2010;100:817–20.
37. Mojumdar SC, Miklovic J, Krutosikova A, Valigura D, Stewart JM. Furopyridines and furopyridine–Ni(II) complexes: synthesis, thermal and spectral characterization. J Therm Anal Calorim. 2005;81:211–5.
38. Vasudevan G, AnbuSrinivasan P, Madhurambal G, Mojumdar SC. Thermal analysis, effect of dopants, spectral characterisation and growth aspects of KAP crystals. J Therm Anal Calorim. 2009;96:99–102.
39. Sawant SY, Kannan KR, Verenkar VMS. Synthesis, characterisation and thermal analysis of nickel manganese fumarato-hydrazinate. In: Pillai CGS, Ramakumar KL, Ravindran PV, Venugopal V, editors. Proceedings of the 13th national symposium on thermal analysis, B.A.R.C. Mumbai: Indian Thermal Analysis Society; 2002. p. 154–5.
40. Jeffery GH, Bassett J, Mendham J, Denney RC. Vogel's text book of quantitative inorganic analysis. 5th ed. London: Longman; 1989.
41. Braibanti A, Dallavalle F, Pellinghelli MA, Leporati E. The Nitrogen–nitrogen stretching band in hydrazine derivatives and complexes. Inorg Chem. 1968;7:1430–3.