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Short communication

Preparation of cobalt ferrite from the thermolysis of cobalt tris(malonato)ferrate(III)trihydrate precursor

B.S. Randhawa [a,*], Manik Gupta [a], Manpreet Kaur [b]

[a] *Department of Chemistry, Guru Nanak Dev University, Amritsar 143005, Punjab, India*
[b] *Layallpur Khalsa College, Jalandhar, Punjab, India*

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Abstract

Thermal decomposition of cobalt tris(malonato)ferrate(III)trihydrate precursor, $Co_3[Fe(CH_2C_2O_4)_3]\cdot 3H_2O$ has been investigated from ambient temperature to 600 °C in static air atmosphere using various physico-chemical techniques, i.e. TG–DTG–DSC, XRD, Mössbauer and IR spectroscopic techniques. The precursor undergoes dehydration and decomposition simultaneously to yield cobalt malonate and iron(II) malonate intermediates at 205 °C. At higher temperature (325 °C) these intermediate species undergo exothermic decomposition to yield CoO and α-Fe_2O_3, respectively. Finally cobalt ferrite, $CoFe_2O_4$, has been obtained as a result of solid–solid reaction between Fe_2O_3 and CoO at a temperature (380 °C) much lower than that of ceramic method. SEM analysis of the final thermolysis product reveals the formation of monodisperse cobalt ferrite nano-particles with an average particle size of 45 nm. Magnetic studies show that these particles have a saturation magnetization of 3095 G and Curie temperature of 504 °C. Lower magnitude of these parameters as compared to the bulk values is attributed to the smaller particle size.

Keywords: A. Calcination; B. X-ray method; D. Ferrites; Mössbauer spectroscopy

1. Introduction

>Ferrites obtained as final thermolysis products from ferricarboxylate precursors find an extensive application as ferrimagnetic materials in microwave devices, digital recording, ferrofluids, sensors, catalysis and magnetic refrigeration systems [1–4]. Spinal ferrites have been regarded as more superior magnetic materials than pure metal due to their high resistivity, higher efficiency and lower cost. Cobalt ferrite finds application in actuators, magneto-optical devices and magnetic recording [5]. The cobalt ferrites in bulk exhibit inverse spinal structure with one half of Fe^{3+} ions in the A sites and the remaining half of Fe^{3+} ions occupying the B sites along with Co^{2+} ions. The magnetic properties of bulk $CoFe_2O_4$ ferrite are found to be sensitive to the distribution of the transition metal ions among the cationic sites in the spinal structure [6]. Preparation of ferrites by precursor method has received immense impetus as it involves intimate blending of the compositional ions at the atomic level, thus resulting in the formation of homogeneous metal ferricarboxylate precursors, which upon thermolysis yield nanosized ferrites. Although detailed investigations have been reported on the thermolysis of transition metal ferrioxalates/maleates [7,8], a similar interest on transition metal ferrimalonates needs to be generated.

2. Experimental procedure

Cobalt tris(malonato)ferrate(III)trihydrate, $Co_3[Fe(CH_2C_2O_4)_3]\cdot 3H_2O$ was prepared by mixing stoichiometric quantities of aqueous solutions of ferric malonate, malonic acid and cobalt carbonate. The reaction mixture was stirred vigorously at 60 °C till a clear solution was obtained. It was then concentrated on water bath and the precipitates of cobalt ferrimalonate precursor were obtained by adding excess of ethanol to it. The precursor was air-dried and stored in vacuum desiccator. The identity of the precursor was established by elemental analysis: [C% = 22.53 (obsd.), 22.62 (calc.); H% = 1.85 (obsd.), 1.88 (calc.); Fe% = 11.65 (obsd), 11.73 (calc.); and Co% = 18.30 (obsd.), 18.53 (calc.)].

The experimental details for recording IR, Mössbauer, XRD powder, SEM and magnetic data are reported elsewhere [9]. For the identification of intermediates and products, the precursor

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* Corresponding author.
E-mail address: balwinderrandhawa@yahoo.co.in (B.S. Randhawa).

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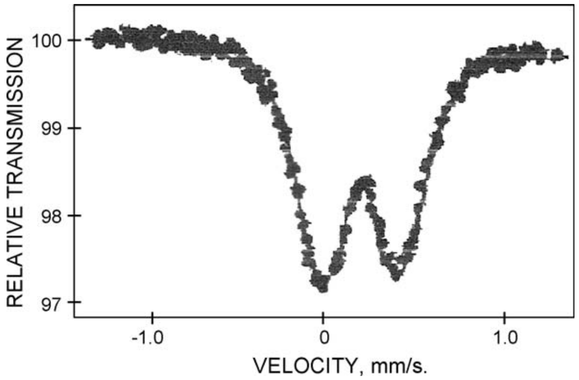

Fig. 1. Mössbauer spectrum of cobalt tris(malonato)ferrate(III)trihydrate precursor at 300 K.

was also calcinated isothermally in nickel crucibles. The variation in temperature was kept at ±5 °C during isothermal calcination.

3. Results and discussion

Infrared (IR) spectra of cobalt tris(malonato)ferrate(III)-trihydrate precursor shows a broad band centered around 3385 cm^{-1} due to ν(O–H) of lattice water. A shoulder at 2910 cm^{-1} is assigned to ν(C–H) of malonate ligand. A broad band centered at 1590 cm^{-1} is due to ν_{asym}(C=O) while band due to ν_{sym}(C=O) lies in the range of 1385–1460 cm^{-1}. Small but distinct bands in the range of 960–1225 $cm-^{1}$ are attributed to ν(C–O), ν(C–C), ν(O–H) bending modes. The bands at 580 and 460 cm^{-1} suggest the presence of Fe–O (carboxylate) bonding [10,11]. Mössbauer spectrum of the precursor exhibits a doublet (Fig. 1) with isomer shift (δ) and quadrupole splitting (Δ) values of 0.37 and 0.49 mms^{-1}, respectively. These parameters agree with those reported for the high spin Fe(III) complexes with octahedral geometry [12]. The coordination number of six for iron is satisfied by three malonate ligands, which bind to iron through oxygen atoms of carboxylate groups. The transition metal ion and water molecules seem to responsible for linking together the complex ion $[Fe(mal)_3]^{3-}$.

Simultaneous TG–DTG–DSC curves of cobalt tris(malonato)ferrate(III)trihydrate precursor at a heating rate of 10 °C min^{-1} are displayed in Fig. 2. A slope in TG (with a mass loss of 16.5%) shows that the dehydration and decomposition of the anhydrous precursor occur simultaneously suggesting the formation of cobalt(II) malonate and iron(II) malonate intermediates at 205 °C (calc. loss = 16.3%). These thermal changes are accompanied by a crescent shaped DTG peak at 190^0C which is endo in DSC with $\Delta H = 426.9$ kJ mol^{-1}. The intermediates have been found to be stable up to 300 °C and the presence of iron(II) malonate has been confirmed by recording Mössbauer parameters of the residue (Table 1) obtained by isothermal calcination of the precursor at 250 °C for 15 min. At higher temperature, the intermediates undergo an abrupt oxidative decomposition as shown by a steep mass loss of 59.8%. This mass loss indicates the complete pyrolysis of the intermediates into CoO and Fe_2O_3 at 325 °C. The corresponding DTG and DSC (exo) peaks lie at 305 °C. This step is highly exothermic as supported by an enthalpy change of −1835.5 kJ mol^{-1}. Mössbauer spectrum of the residue obtained at 325 °C showed a six line pattern, the parameters of which resemble to those reported for α-Fe_2O_3 [13]. As heating continues, a solid state reaction between Fe_2O_3 and CoO results in the formation of cobalt ferrite; $CoFe_2O_4$ at 380 °C as supported by an exotherm in DSC with $\Delta H = -420.2$ kJ mol^{-1}. Mössbauer spectrum of the final thermolysis residue (Fig. 3) exhibits two overlapping sextets, the parameters (Table 1) of which agree with those reported for cobalt ferrite, $CoFe_2O_4$ [14]. The presence of $CoFe_2O_4$ has been further confirmed by recording XRD powder pattern (Fig. 4) of

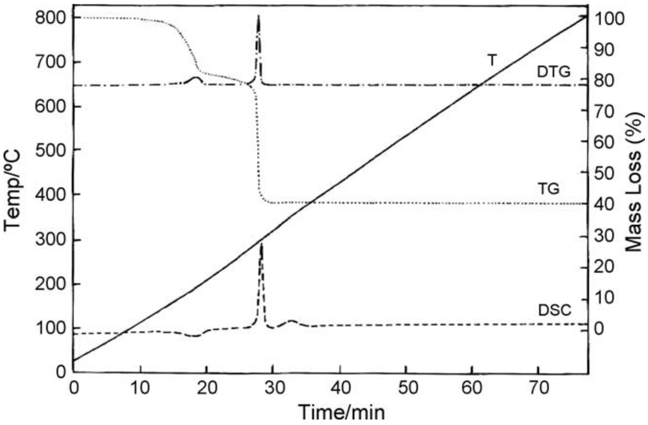

Fig. 2. Simultaneous TG–DTG–DSC thermograph of cobalt tris(malonato)-ferrate(III)trihydrate precursor.

Table 1
Mössbauer parameters of the thermolysis products of $Co_3[Fe(mal)_3]_2·3H_2O$ recorded at 77 K.

Calcining temp. (°C)	δ (mm s^{-1})[a]	Δ (mms^{-1})	B (T)	Cationic (Fe^{3+}) distribution	Assignment
250	1.35	1.78	–	–	$Fe^{II}CH_2C_2O_4$
325	0.49	0.02	53.8	–	α-Fe_2O_3
380	0.48	–	53.3	26% (oct)	$CoFe_2O_4$
	0.39	–	49.7	74% (tet)	

[a] w.r.t. pure iron absorber, B: internal magnetic field in Tesla, oct: octahedral site, tet: tetrahedral site.

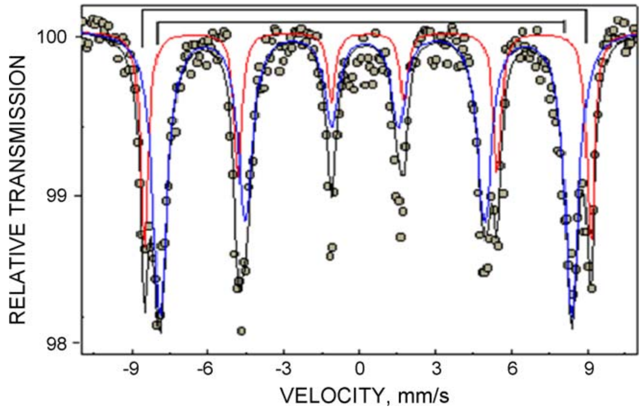

Fig. 3. Mossbauer spectrum of final thermolysis residue of cobalt tris(malonato)ferrate(III)hydrate.

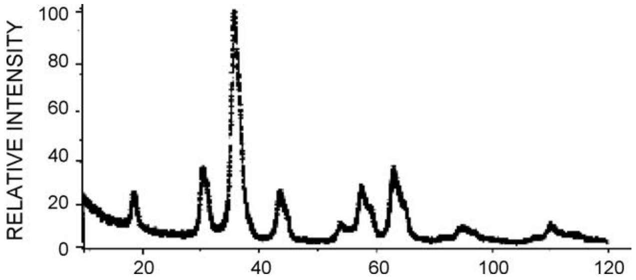

Fig. 4. XRD powder pattern of the final thermolysis product after treating with dilute HNO_3.

Table 2
Magnetic properties of $CoFe_2O_4$ obtained.

Density (g/cm^3)	Saturation magnetization (G)	Specific magnetization (G/cm^3)	Curie temperature (T_c) (°C)	Average grain size (nm)
4.46	3095	694	504	45

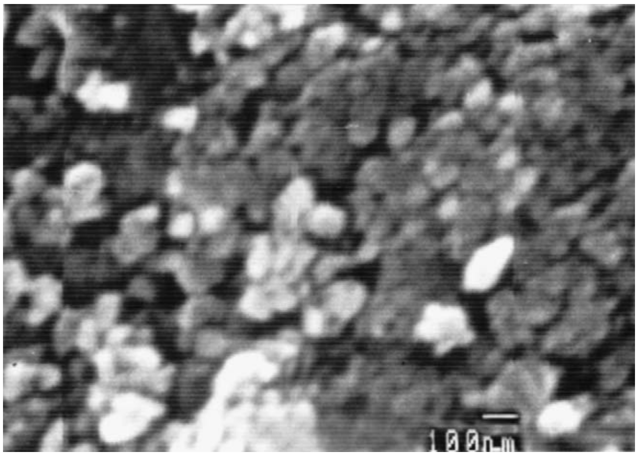

Fig. 5. SEM micrograph of the final thermolysis product of cobalt ferrimalonate.

the ultimate product [15]. The magnetic parameters for cobalt ferrite (Table 2) show that ferrite particles prepared from malonate precursor have higher value of saturation magnetization and Curie temperature as compared to those obtained from respective ferrioxalates. The SEM micrograph (Fig. 5) reveals the formation of monodisperse ferrite particles with an average particle diameter of 45 nm.

On the basis of various physico-chemical studies, following mechanism for the aerial thermolysis of cobalt ferrimalonate is proposed:

$$Co_3[Fe(CH_2C_2O_4)_3]_2 \cdot 3H_2O \xrightarrow{205\,^{\circ}C} 3CoCH_2C_2O_4 + 2FeCH_2C_2O_4 + \text{gaseous products}$$

$$3CoCH_2C_2O_4 + 2FeCH_2C_2O_4 \xrightarrow{325\,^{\circ}C} 3CoO + \alpha\text{-}Fe_2O_3 + \text{gaseous products}$$

$$3CoO + \alpha\text{-}Fe_2O_3 \xrightarrow{380\,^{\circ}C} CoFe_2O_4 + 2CoO$$

In order to get pure ferrite, i.e. $CoFe_2O_4$, the end product was treated with 2N HNO_3 to remove CoO.

4. Conclusions

From various physico-chemical studies performed during the aerial thermolysis of cobalt tris(malonato)ferrate(III)trihydrate precursor, the following conclusions can be drawn:

(A) The thermal decomposition occurs in three major consecutive steps:
  (1) Simultaneous dehydration and decomposition of the precursor into cobalt malonate and iron(II) malonate intermediates at 205 °C.
  (2) Exothermic decomposition of the intermediates into respective oxides, i.e. CoO and Fe_2O_3 at 325 °C.
  (3) A solid state reaction between the oxides to yield cobalt ferrite at 380 °C.

(B) The transition metal malonate, obtained during course of decomposition of corresponding transition metal ferrimalonate, decomposes at lower temperature than the pure malonate, due to catalytic effect of α-Fe_2O_3 present.

(C) The temperature of ferrite formation is much lower than that of alkali/alkaline earth metal–ferrimalonates. This is due to the direct decomposition of former into the oxide phase (without yielding carbonate as intermediate). The temperature of ferrite formation (380 °C) is considerably lower than that of conventional ceramic method (>10,00 °C).

(D) The ferrites obtained exhibits promising values of magnetic parameters, i.e. saturation magnetization, Curie temperature, etc., exploring its suitability for functioning at high/microwave frequencies.

(E) Another attractive feature of the technique employed is that it does not involve any milling of the starting material. Milling introduces lattice defects and strains in the ferrites obtained, thus affecting their permanent magnetic properties.

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