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THERMAL ANALYSIS OF MAGNESIUM TRIS(MALEATO) FERRATE(III) DODECAHYDRATE
Physico-chemical studies

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Abstract

Thermal analysis of magnesium tris(maleato) ferrate(III) dodecahydrate has been studied from ambient to 700°C in static air atmosphere employing TG, DTG, DTA, XRD, Mössbauer and infrared spectroscopic techniques. The precursor decomposes to iron(II) intermediate species along with magnesium maleate at 248°C. The iron(II) species then undergo oxidative decomposition to give α-Fe_2O_3 at 400°C. At higher temperatures magnesium maleate decomposes directly to magnesium oxide, MgO, which undergoes a solid state reaction with α-Fe_2O_3 to yield magnesium ferrite ($MgFe_2O_4$) at 600°C, a temperature much lower than for ceramic method. The results have been compared with those of the oxalate precursor.

Keywords: DTA, DTG, ferrites, magnesium, Mössbauer spectra, TG, XRD

Introduction

Ferrites obtained from the thermal decomposition of various iron(III)carboxylate precursors have attracted much attention not only as permanent magnets and microwave devices, but also as a promising material for magnetic recording medium [1]. Ferrites of pure/manganese doped magnesium have found extensive application in computer storage systems and switching circuits [2]. Magnesium ferrite has been prepared [3] by ceramic method which involves milling of the reactants which imparts defects and strains in the product. Alternatively magnesium ferrite has been obtained from thermal decomposition of the precursor, magnesium tris(oxalato) ferrate(III), which in turn is synthesised by the liquid-mix technique [4]. This technique does not involve milling of the reactants and ferrites are obtained at lower temperatures in shorter time than in the conventional ceramic method. The present investigation of magnesium tris(maleato) ferrate(III) has been undertaken to get ferrite at minimum possible temperature and compare its thermal stability with respective oxalate complex.

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Materials and methods

Magnesium tris(maleato) ferrate(III) dodecahydrate was prepared by mixing stoichiometric quantities of aqueous solutions of ferric maleate, magnesium carbonate and maleic acid. The reaction mixture was stirred vigorously and concentrated on a water bath until a brown coloured product is formed after the addition of excess acetone. The identity of the complex was established by chemical analysis. The content of iron was determined spectrophotometrically using 1,10-phenanthroline method [5]. (Found: Fe 10.91, C 27.08, H 3.01%; calc.: Fe 10.30, C 26.56, H 3.32%).

IR spectra were recorded in KBr matrix on a Pye-Unicam IR spectrophotometer in the range 4000–200 cm^{-1}. Thermal analysis was performed at USIC, University of Roorkee, Roorkee on Stanton Redcraft (STA-780) in static air atmosphere at a heating rate of 10°C min^{-1}. XRD powder patterns were also recorded using Ni filtered CuK_α radiation. The experimental details of Mössbauer investigation were as reported elsewhere [6]. The isomer shift values are reported w.r.t. pure iron absorber.

Results and discussion

The IR spectrum of magnesium tris(maleato) ferrate(III) dodecahydrate shows a broad band centred at 3290 cm^{-1} due to ν(OH) of lattice water and a distinct shoulder at 2910 cm^{-1} due to ν(C–H) of the maleate group. The overlapping bands due to ν(C=C) and ν_{asy}(C=O) lie in the range 1570–1650 cm^{-1}. Bands at 1435 and 1230 cm^{-1} are attributed to ν_{sym}(C=O) of the coordinated carboxylate group [7]. Sharp band at 860 cm^{-1} is assigned to *cis* (C–H) wagging. Small distinct band at 530 cm^{-1} indicates the presence of Fe–O (carboxylate) bonding [8].

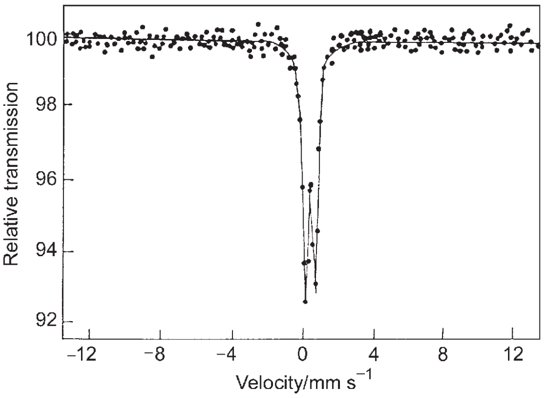

Fig. 1 Mössbauer spectrum of magnesium tris(maleato) ferrate(III) dodecahydrate at 25±2°C

Mössbauer spectrum of magnesium tris(maleato) ferrate(III) dodecahydrate at 300 K exhibits a doublet (Fig. 1) with isomer shift and quadrupole splitting values of 0.41 and 0.56 mm s^{-1} respectively. These parameters are in agreement with those re-

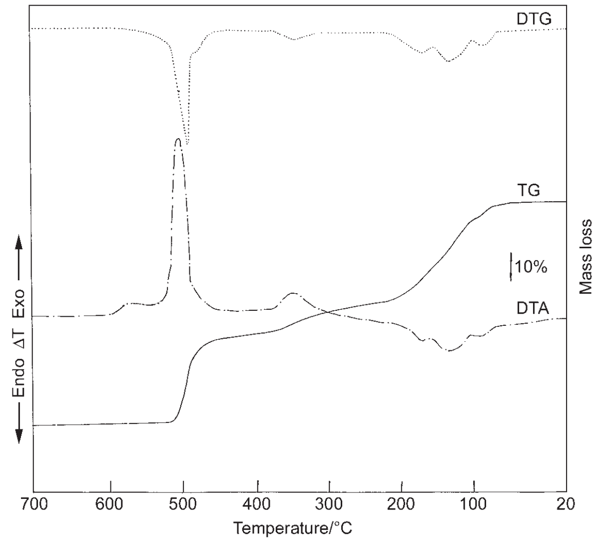

Fig. 2 Simultaneous TG–DTG–DTA curves of magnesium tris(maleato) ferrate(III) dodecahydrate

ported for high spin iron(III) complexes having octahedral geometry [9]. The high spin nature of the complex has also been confirmed by its μ_{eff} value of 5.87 B.M.

Figure 2 shows the simultaneous TG–DTA–DTG curves for magnesium tris(maleato) ferrate(III) at a heating rate of 10°C min^{-1}. DTA shows three consecutive endothermic stages with peak temperatures at 97, 140 and 180°C respectively. These stages are also revealed in TG and DTG curves. The first two stages are associated with the dehydration which completes at 170°C as indicated by a mass loss of 20% (calc. loss=19.9%). The third stage is due to the decomposition of anhydrous complex into

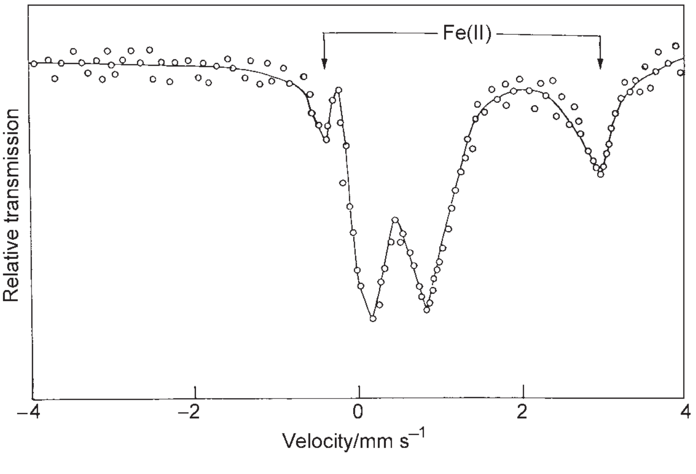

Fig. 3 Mössbauer spectrum of magnesium iron(III) maleate heated at 250°C

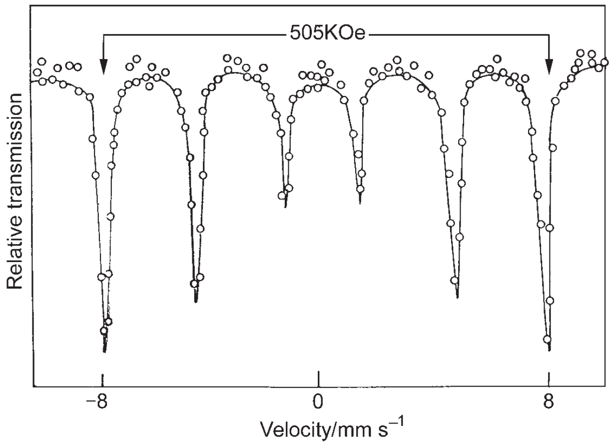

Fig. 4 Mössbauer spectrum of magnesium iron(III) maleate calcined at 400°C

magnesium maleate and iron(II) oxalate as shown by a mass loss of 35% (calc. loss=35%) at 248°C. Mössbauer spectrum of the parent complex calcined isothermally at 250°C for 15 min shows two quadrupole doublets (Fig. 3) one with isomer shift and quadrupole splitting values of 1.20 and 2.58 mm s^{-1} respectively indicating the formation of iron(II) oxalate [10] and the other doublet is due to the parent complex. As heating continues, TG curve slackens until a mass loss of 46% is reached at 400°C indicating the oxidative decomposition of iron(II) oxalate into iron(III) oxide along with magnesium maleate. The corresponding DTG and DTA(exo) peaks both lie at 360°C. The Mössbauer spectrum of the residue obtained from the parent complex after heating at 400°C for 2 h exhibits a six-line pattern (Fig. 4) with isomer shift and internal magnetic field values of 0.44 mm s^{-1} and 505 KOe respectively. These parameters are in close agreement with those reported [11, 12] for α-Fe_2O_3.

Table 1 Mössbauer parameters for the thermal analysis products of $Mg_3[Fe(C_2H_2C_2O_4)_3]_2 \cdot 12H_2O$ at 300 K

Temperature of calcination/°C	δ/ mm s^{-1}	Δ_{EQ}/ mm s^{-1}	*HI*/ KOe	Cationic(Fe^{3+}) distribution/%	Assignment
250	1.20	2.58	–	–	$Fe^{II}C_2O_4$
–	0.40	0.68	–	–	parent complex
400	0.44	–	505	–	α-Fe_2O_3
600	0.38	0.20	517	36	α-Fe_2O_3
–	0.36	0.01	493	25	$MgFe_2O_4$
–	0.27	–	467	39	–
–	0.47	0.34	543	41	α-Fe_2O_3 (77 K)
–	0.44	0.12	527	27	$MgFe_2O_4$ (77 K)
–	0.34	0.02	508	32	–

Further, there is a strong exotherm at 510°C corresponding to a mass loss of 74.5% (calc. loss=74.16%) marking the formation of magnesium oxide from magnesium maleate through an intermediate step in which magnesium oxalate is formed as shown by a shoulder in the respective DTG peak. The liberation of acetylene from maleate to yield oxalate has been reported during ‘Kolbe electrolysis’ of metal maleate/fumarate in solution phase [13, 14]. Magnesium maleate formed decomposes at much lower temperature (410°C) as compared to its pure salt [15] (450°C) due to the (i) metastable structure of the former and (ii) catalytic effect of α-Fe_2O_3 present. Neither TG nor IR spectrum indicates the presence of magnesium carbonate at any stage and thus the decomposition of mixed maleate resembles that of magnesium oxalate/malonate which also directly yield oxide [16, 17]. As heating continued, solid state reaction between the oxides of magnesium and iron occurred as revealed by the exotherm in DTA, resulting in magnesium ferrite, $MgFe_2O_4$. The presence of this product has been affirmed by Mössbauer spectrum of the final residue of analyses (Fig. 5). Mössbauer spectrum displays three different oxide phases, the parameters of which (recorded at 77 and 300 K) are listed in Table 1. The parameters of the outer sextet correspond to α-Fe_2O_3 while those of the inner ones [18] are assigned to $MgFe_2O_4$. The cationic distribution of this ferroimagnetic spinel in octahedral and tetrahedral sites have been found to be 25 and 39% respectively.

XRD data of the final thermal analysis product (listed in Table 2) also confirms the formation of ferrite.

Table 2 Room temperature XRD powder pattern of the thermal analysis residue of magnesium tris(maleato) ferrate(III) dodecahydrate at 600°C

2θ	*d*/Å	Relative intensity	Assignment
18.20	4.870	23	$MgFe_2O_4$[a]
30.17	2.960	26	$MgFe_2O_4$
33.28	2.692	39	α-Fe_2O_3[b]
35.60	2.520	63	$MgFe_2O_4$
37.00	2.420	25	$MgFe_2O_4$, MgO[c]
40.80	2.210	18	α-Fe_2O_3
43.04	2.101	100	$MgFe_2O_4$
49.54	1.840	22	α-Fe_2O_3
54.00	1.697	20	MgO, $MgFe_2O_4$
57.00	1.613	25	$MgFe_2O_4$

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In the light of the above results, the following thermal decomposition scheme is proposed for magnesium tris(maleato) ferrate(III) dodecahydrate:

$$Mg_3[Fe(C_2H_2C_2O_4)_3]_2\cdot 12H_2O \xrightarrow{115°C} Mg_3[Fe(C_2H_2C_2O_4)_3]_2\cdot 8H_2O+4H_2O(g)$$

$$Mg_3[Fe(C_2H_2C_2O_4)_3]_2\cdot 8H_2O \xrightarrow{170°C} Mg_3[Fe(C_2H_2C_2O_4)_3]_2+8H_2O(g)$$

$$Mg_3[Fe(C_2H_2C_2O_4)_3]_2 \xrightarrow{248\,°C} 3MgC_2H_2C_2O_4{+}2Fe^{II}C_2O_4{+}3C_2H_2(g){+}2CO_2(g)$$

$$2Fe^{II}C_2O_4 \xrightarrow{400\,°C} \alpha\text{-}Fe_2O_3{+}3CO(g){+}CO_2(g)$$

$$3MgC_2H_2C_2O_4 \xrightarrow{470-530\,°C} 3MgO\text{+gaseous products}$$

$$\alpha\text{-}Fe_2O_3{+}3MgO \xrightarrow{530-600\,°C} MgFe_2O_4{+}2MgO$$

Thus the maleate complex, i.e. seven-membered chelate decomposes at a lower temperature (170°C) than the respective five-membered chelate i.e. oxalate complex [4] (200°C). It can be explained on the basis of high temperature acid-base theory – the weaker the anion base is the higher the temperature of decomposition [19] is; oxalate ion is a weaker anion base than maleate ion. Irving *et al.* [20] have also studied the influence of ring size upon the stability of metal chelates and have generalized that the stability of chelate complexes decreases with increasing ring size. Decrease in stability with increasing chain length of the ligand has been explained, to a large extent, on the basis of chelate/entropy factor.

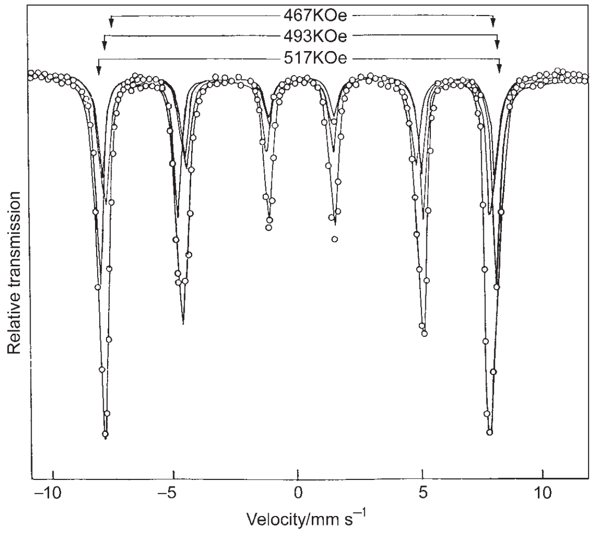

Fig. 5 Mössbauer spectrum of the final thermal analysis product of magnesium iron(III) maleate at 300 K

An attractive feature of the precursor technique undertaken is the preparation of ferrite (end product) at a temperature much lower than that of conventional ceramic method (>1000°C). It is even lower than the temperature for ferrite formation (700°C) from the thermolysis of respective oxalate precursor [4]. These studies are important because of the extensive application of ferrites as device materials in recording and microwave appliances.

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