

Calcium ferrite formation from the thermolysis of calcium tris (maleato) ferrate(III)[†]

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Abstract. For preparing calcium ferrite, calcium tris (maleato) ferrate(III) precursor was prepared by mixing aqueous solutions of iron(III) maleate, calcium maleate and maleic acid. Various physico-chemical techniques i.e. TG, DTG, DTA, Mössbauer, XRD, IR etc have been used to study the decomposition behaviour from ambient to 900°C and ferrite formation. Three consecutive decomposition steps leading to the formation of α -Fe₂O₃ and calcium carbonate have been observed at various stages of thermolysis. In the final stage the ferrite, Ca₂Fe₂O₅, is obtained as a result of solid state reaction between α -Fe₂O₃ and calcium carbonate at 788°C, a temperature much lower than for ceramic method. The results have been compared with those of the oxalate precursor.

Keywords. Ferrites; thermal decomposition; precursor technique; calcium ferrimaleate.

1. Introduction

Because of their extensive application in radio, television, microwave and satellite communication, bubble devices, audio-video, digital recording and as permanent magnets (Viswanathan and Murthy 1990), ferrites have opened a new vista in the field of chemical physics of materials. Keeping in view these technological applications, ferrites have been regarded as an important class of magnetic materials. The excellent combination of electrical and magnetic characteristics apart from the appreciable temperature performance have made the ferrite materials highly suitable for microwave application. Since the formation of ferrites by the conventional ceramic method has several disadvantages viz. nonhomogeneity, large particle size, low surface area and poor sinterability, the precursor technique has been successfully applied for the preparation of ferrites (Bassi *et al* 1989; Randhawa *et al* 1996; Randhawa and Sweety 1998). This method involves the preparation of precursor (metal ferricarboxylate) by chemical means and its decomposition into ferrites.

2. Experimental

Calcium tris (maleato) ferrate(III) was prepared by mixing stoichiometric quantities of aqueous solutions of calcium maleate, iron(III) maleate and maleic acid. The reaction mixture was concentrated on a water bath until a brown coloured product formed after the addition of excess of acetone. The complex was vacuum dried and its identity

was established by chemical analysis. The infrared (IR) spectra of the complex and products were recorded on Pye–Unicam SP3-300 IR spectrophotometer in the range 4000–200 cm⁻¹ using KBr pellet technique. Simultaneous TG, DTG and DTA curves were recorded on Stanton Redcroft STA-780 at a heating rate of 10° mm⁻¹. XRD powder pattern was recorded at USIC, University of Roorkee, Roorkee. Mössbauer measurements were made at laboratoire de physique de l'état condensé, CNRS, France. All the spectra were fitted to the Lorentzian shape. The isomer shift values are reported with respect to pure iron absorber.

3. Results and discussion

The IR spectrum of calcium tris (maleato) ferrate(III) shows a small but distinct band at about 2850 cm⁻¹ due to ν (C–H) of the maleate group. A broad band centred at about 1620 cm⁻¹ due to overlapping of ν (C=C) and ν_{asy} (C=O) has been observed. Bands in the range 1435–1315 cm⁻¹ indicate ν_{sym} (C=O) of the coordinated carboxylate group (Nakamoto 1970). A sharp band at 860 cm⁻¹ is assigned to cis(C–H) wagging while another distinct band at 560 cm⁻¹ reveals the presence of Fe–O (carboxylate) bonding (Ferraro *et al* 1967), Mössbauer spectrum of the precursor at 300 K displays a doublet with isomer shift and quadrupole splitting values of 0.41 and 0.68 mm s⁻¹ respectively. These parameters agree with those reported for high spin Fe(III) complexes with octahedral geometry (Vertes *et al* 1979). The six-coordination number of iron is satisfied by three maleate ligands which are bound through oxygen atoms of the carboxyl group.

Figure 1 shows the simultaneous thermograms (TG, DTG, DTA) of calcium tris (maleato) ferrate(III) at a

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heating rate of $10^{\circ} \text{ min}^{-1}$. The complex is anhydrous and starts decomposing at 170° C until a mass loss of 18% is reached at 310° C indicating the formation of iron(II) maleate and calcium maleate (calc. loss 18.1%). DTG shows a respective peak at 237° C . The iron(II) species could not be detected due to its instability. It was formed in an endostep which subsequently becomes exo in a continuously heated system and hence undergoes oxidative decomposition to yield Fe_2O_3 at a mass loss of 34% at 360° C (calc. loss 32.09%). The respective DTG peak exists at 330° C .

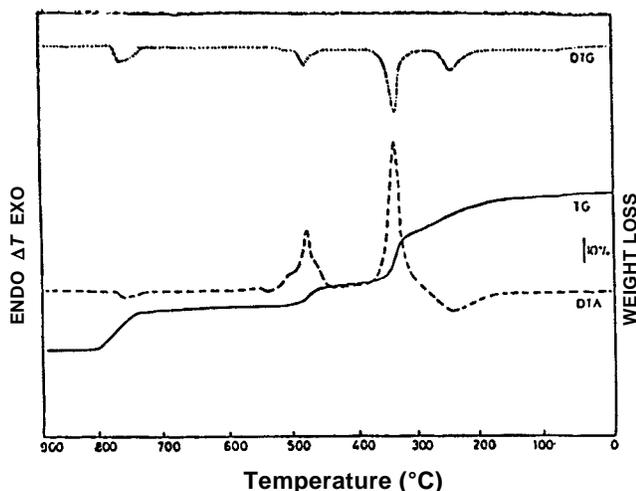


Figure 1. STA curves of the maleato complex at a heating rate of $10^{\circ} \text{ min}^{-1}$.

The existence of Fe_2O_3 has been confirmed by the Mössbauer spectrum of the residue obtained by calcining the parent complex isothermally at 360° C for 1 h. The sextet obtained at 77 K (figure 2) in the spectrum with isomer shift and internal magnetic field values of 0.46 mm sec^{-1} and 542 KOe, respectively agree with those reported for $\alpha\text{-Fe}_2\text{O}_3$ (Cox *et al* 1962). An arrest in TG curve at a mass loss of 48% suggests the formation of calcium carbonate (calc. loss 49.7%) through an intermediate step in which calcium oxalate is formed. These thermal changes are accompanied by the overlapping peaks in DTA (exo) and DTG thermograms. Calcium carbonate thus formed remains stable up to 720° C , and then undergoes a solid–solid reaction with $\alpha\text{-Fe}_2\text{O}_3$ to form calcium ferrite i.e. $\text{Ca}_2\text{Fe}_2\text{O}_5$, with the evolution of CO_2 as revealed by a characteristic endotherm at 745° C . The identity of the final thermolysis product as $\text{Ca}_2\text{Fe}_2\text{O}_5$ has been confirmed by its Mössbauer spectra recorded both at 77 K (figure 3) and 300 K each exhibiting two overlapping sextets due to the distribution of Fe^{3+} in octahedral and tetrahedral sites. The parameters of the sextets, listed in table 1, resemble to those reported for $\text{Ca}_2\text{Fe}_2\text{O}_5$ (Greenwood and Gibb 1971; Grenier *et al* 1997). The higher internal magnetic field values at 77 K as compared to 300 K are expected as the magnitude of this parameter is temperature dependent (Bhide 1973; Kulkarni *et al* 1994).

The ferrite has been obtained at a much lower temperature (788° C) and also in a shorter time interval as compared to that of the ceramic method. This temperature of ferrite formation is even lower than that of the one obtained from the thermolysis of oxalate/malonate precursors ($> 800^{\circ} \text{ C}$). Another attractive feature of the method

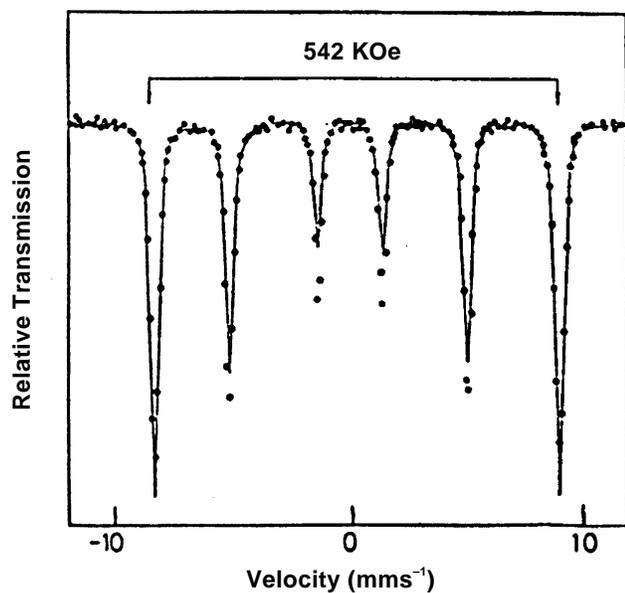


Figure 2. Mössbauer spectrum of the residue obtained at 360° C .

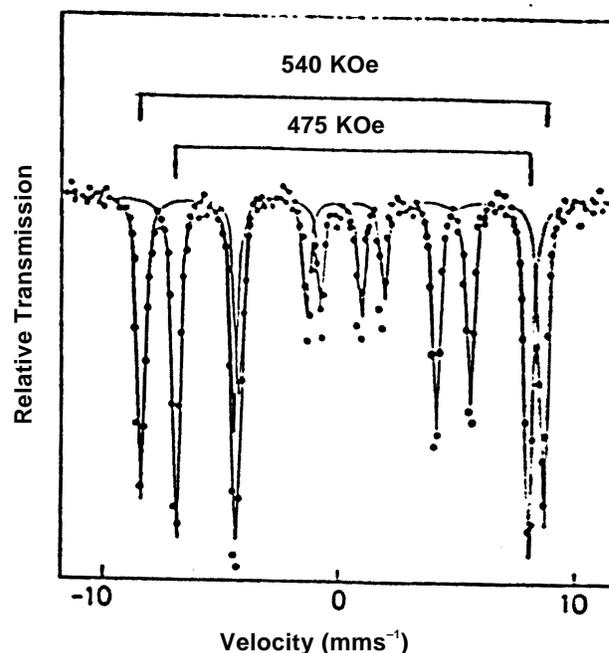


Figure 3. Mössbauer spectrum of the final thermolysis product.

Table 1. Mössbauer parameters for thermolysis products of $\text{Ca}_3[\text{Fe}(\text{OX})_3]_2$ at 77 K.

Heating temp. (°C)	δ (mms^{-1})	ΔEQ (mms^{-1})	HI (KOe)	Fe^3 (Distr. %)	Assignment
360	0.46	–	542	–	$\alpha\text{-Fe}_2\text{O}_3$
800	0.46	– 0.52	540	47.4 (oct)	$\text{Ca}_2\text{Fe}_2\text{O}_5$
	0.27	0.71	475	52.6 (tet)	
	0.37	– 0.52	504	45 (oct)	
	0.18	0.72	429	55 (tet)	$\text{Ca}_2\text{Fe}_2\text{O}_5^*$

*Recorded at 300 K.

Table 2. XRD data for the final thermolysis product.

$d(\text{\AA})$	I/I_0	Assignment
3.478	34	$\text{Ca}_2\text{Fe}_2\text{O}_5^a$
2.693	10	$\text{Ca}_2\text{Fe}_2\text{O}_5$
2.666	20	$\text{Ca}_2\text{Fe}_2\text{O}_5$
2.391	10	$\text{Ca}_2\text{Fe}_2\text{O}_5$
2.192	22	$\text{Ca}_2\text{Fe}_2\text{O}_5$
2.075	5	$\text{Ca}_2\text{Fe}_2\text{O}_5$
2.070	100	$\text{Ca}_2\text{Fe}_2\text{O}_5, \text{CaO}^b$
1.928	10	$\text{Ca}_2\text{Fe}_2\text{O}_5$
1.876	8	$\text{Ca}_2\text{Fe}_2\text{O}_5$
1.844	8	$\text{Ca}_2\text{Fe}_2\text{O}_5$
1.744	6	$\text{Ca}_2\text{Fe}_2\text{O}_5$
1.644	6	$\text{Ca}_2\text{Fe}_2\text{O}_5$
1.394	6	$\text{Ca}_2\text{Fe}_2\text{O}_5$
1.398	5	$\text{Ca}_2\text{Fe}_2\text{O}_5$

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used is that it does not involve milling of the precursor which is necessary in the conventional ceramic method. The milling introduces defects and strains in ferrite obtained which in turn affects its permanent magnetic properties.

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