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PHYSICO-CHEMICAL STUDIES ON ZINC HEXA(FORMATO)FERRATE(III) DECAHYDRATE

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Abstract

Thermal analysis of zinc hexa(formato)ferrate(III) decahydrate, $Zn_3[Fe(HCOO)_6]_2 \cdot 10H_2O$ has been investigated upto 800°C in static air atmosphere employing TG, DSC, XRD, IR, ESR and Mössbauer spectroscopic techniques. After dehydration at 160°C, the anhydrous complex decomposes into α-Fe_2O_3 and zinc carbonate in successive stages. Subsequently the cations remix to yield fine particles of zinc ferrite, $ZnFe_2O_4$, as a result of solid state reaction between α-Fe_2O_3 and zinc carbonate at a temperature (600°C) much lower than for ceramic method.

Keywords: DSC, ferrite, Mössbauer spectra, TG, thermal decomposition, zinc ferriformate

Introduction

Because of their extensive application in radio, television, microwave and satellite communication, bubble devices, audio-video digital recording and as permanent magnets, the ferrites have opened a new vista in the field of chemical physics of materials and the need of high resistivity ferrites led to the synthesis of various ferrites. The advantage with the ferrites over the pure metals is that they yield higher efficiency, lower costs, greater uniformity and easier manufacture [1]. Keeping in view the technological applications of zinc ferrites as recording head, transformer cores, microwave devices etc, thermolysis of zinc ferriformate precursor has been undertaken for the obtention of zinc ferrite. Since the conventional ceramic method for the preparation of ferrites imparts defects and strains in the product (ferrite) the precursor method has been employed. We have already applied this method for the obtention of various ferrites [2–3].

Experimental

Zinc hexa(formato)ferrate(III) hexahydrate i.e. $Zn_3[Fe(HCOO)_6]_2 \cdot 10H_2O$ was prepared by mixing stoichiometric quantities of aqueous solutions of ferric chloride, zinc formate and formic acid. The reaction mixture was stirred vigorously and then concentrated on water bath until a brown coloured product formed. The brown product

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was filtered and washed with cold water and dried in air. The identity of the complex (precursor) was established by chemical analysis:

	C/%	H/%	Fe/%	Zn/%
Observed	13.11	2.36	10.23	18.11
Calculated	14.02	3.11	10.90	19.06

The percentage of iron was determined spectrophotometrically using 1,10-phenanthroline [4]. The zinc content was determined electrogravimetrically after complexing the iron content (present in the complex) with 1,10-phenanthroline [4] and then precipitating it by adding ethanol in excess. The red precipitates were filtered out and the filtrate was subjected to electrogravimetric analysis [5] for estimation of zinc content using platinum electrode.

The infrared spectra of the complex and products were recorded on Pyeunicam SP3-300 IR spectrophotometer in the range 4000–200 cm^{-1} using KBr pellets as reference. Simultaneous TG and DSC curves were recorded on Mettler TG-50 at a heating rate of 10°C min^{-1} in static air atmosphere. ESR spectrum was recorded on ESR spectrometer JES-FE 3xG. Mössbauer and XRD measurements were performed at USIC, UOR, Roorkee. The isomer shift values have been reported w.r.t. pure iron absorber.

Results and discussion

The infrared spectrum of zinc hexa(formato)ferrate(III) decahydrate shows a broad band near 3310 cm^{-1} due to ν(O–H) of lattice water, a small but distinct band at about 2900 cm^{-1} due to ν(C–H), a broad band around 1630 cm^{-1} due to ν_{asy}(C=O) and a strong band at 1380 cm^{-1} due to ν_{sym}(C=O) of the coordinated carboxylate groups. Small but distinct bands at 580 and 400 cm^{-1} due to ν(Fe–O) suggest the presence of Fe–O (carboxylate) bonding [6].

The six co-ordination number of iron is satisfied by six formate ligands which are bound through oxygen atoms of the carboxyl groups. Zinc and water molecules seem to be responsible for linking together the complex ion [7]. A ‘g’ value of 2.0 from the ESR spectrum indicates the presence of high spin iron(III) nature of the complex. The high spin nature of the iron(III) moiety has also been confirmed by the μ_{eff} value of 5.98 B.M.

Figure 1 shows the simultaneous TG and DSC curves of zinc hexa(formato)-ferrate(III) decahydrate at a heating rate of 10°C min^{-1}. Dehydration is complete at 160°C as shown by a plateau in TG at a mass loss of 17.50% due to the removal of ten water molecules (calc. loss=18.45%). DSC curve exhibits an endotherm at 95°C showing a ΔH value of 366.33 kJ mol^{-1} for dehydration. Immediately after the dehydration, the anhydrous complex starts decomposing till a mass loss of 55.47% is obtained in TG at 320°C indicating the formation of Fe_2O_3 and ZnO (calc. loss= 60.75%). The decomposition of zinc formate directly into zinc oxide has been reported in literature [8]. A comparison of the experimental and calculated mass losses suggests the presence of some elemental car-

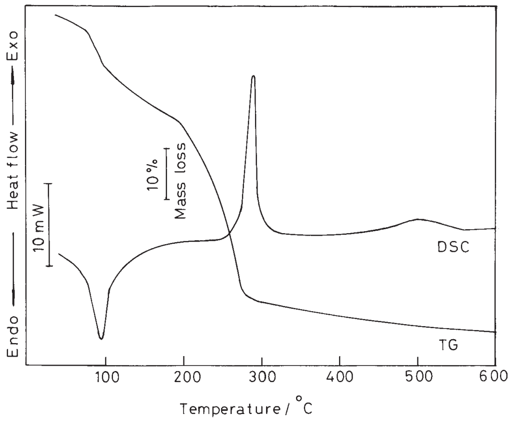

Fig. 1 Simultaneous TG and DSC curves for zinc hexa(formato)ferrate(III) decahydrate at a heating rate of 10°C min^{-1}

bon left unoxidized in the solid mixture (Fe_2O_3, ZnO). The presence of free carbon has been confirmed in the black residue obtained by calcining the parent complex isothermally at 320°C for 20 min. DSC curve shows the corresponding exotherm at 290°C with a ΔH value of 351.34 kJ mol^{-1}. The formation of Fe_2O_3 has been revealed by the presence of a symmetrical sextet in the Mössbauer spectrum (Fig. 2) of the residue. The isomer shift and internal magnetic field values of 0.40 mm s^{-1} and 510 KOe respectively of the sextet agree with the reported values [9–10] for α-Fe_2O_3. The infrared spectrum of the residue shows small but distinct bands at 550, 440 and 320 cm^{-1} due to ν(M–O) of iron/zinc oxide [6].

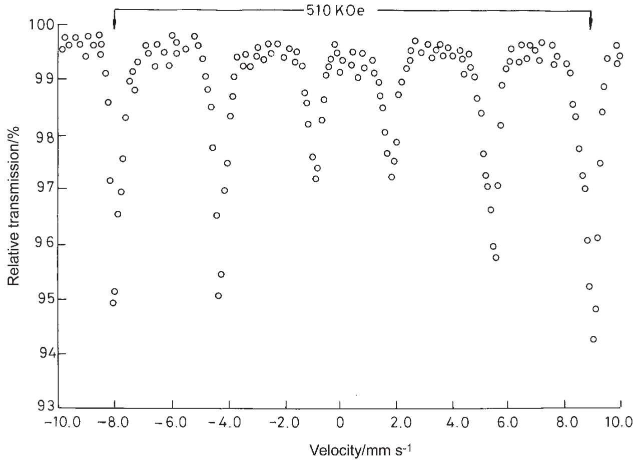

Fig. 2 Mössbauer spectrum of zinc hexa(formato)ferrate(III) decahydrate calcined at 300°C for 2 h

At higher temperature a solid state reaction between α-Fe_2O_3 and ZnO occurs to yield the ferrite ($ZnFe_2O_4$) at 600°C while the free carbon takes up oxygen to escape as carbon dioxide/carbon monoxide. TG shows a final mass loss of 61.4% due to the formation of $ZnFe_2O_4$ (calc. loss=60.75%). There exists a corresponding exotherm in DSC for this process. Unlike other transition metal ferrites (Mn, Co, Ni), final residue does not show any Curie temperature because the Zn^{2+} ion is non-magnetic. Mössbauer spectrum of the final thermolysis product exhibits a doublet (Fig. 3) with isomer shift and quadrupole splitting values of 0.20 and 0.45 mm s^{-1} respectively. These parameters are in good agreement with those reported [11, 12] for zinc ferrite, $ZnFe_2O_4$. This ferrite is a normal spinel with Zn^{2+} ions in the tetrahedral (A) site and both the Fe^{3+} ions occupying the octahedral (B) sites. There can be neither A–B interaction nor A–A interaction, since Zn^{2+} is a non-magnetic ion. The only prevalent magnetic interaction is B–B interaction between the Fe^{3+} ions, which is antiferromagnetic [1]. The existence of $ZnFe_2O_4$ has also been confirmed by the XRD powder pattern of the final thermolysis residue (Fig. 4).

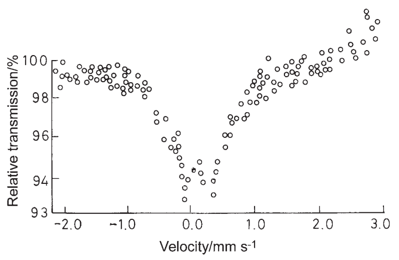

Fig. 3 Mössbauer spectrum of the final thermolysis product

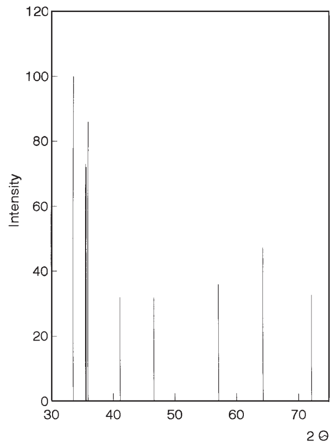

Fig. 4 XRD powder pattern of the final thermolysis product

On the basis of various physico-chemical studies the following three major consecutive steps for the aerial decomposition of zinc ferriformate decahydrate are proposed:

i) dehydration of the complex at 160°C;
ii) decomposition of the anhydrous complex into α-Fe_2O_3 and ZnO, at 320°C;
iii) a solid state reaction between α-Fe_2O_3 and ZnO to yield $ZnFe_2O_4$ at 600°C.

The ferrite ($ZnFe_2O_4$) has been obtained at a temperature (600°C) much lower than for ceramic method [13, 14]. Another attracting feature of the method used is that it does not involve milling of the complex (precursor) which is necessary in the ceramic method and imparts lattice defects and strains in the ferrite obtained [15].

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