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THERMOANALYTICAL STUDY OF Cu–Mg–Zn FERRITES

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Abstract

Homogeneous solid solution oxalates of Fe^{2+}, Cu^{2+}, Mg^{2+} and Zn^{2+} metals were prepared by co-precipitation from respective metal acetate solutions with oxalic acid solution. The thermogravimetric (TG) analysis of co-precipitated oxalate complexes with general formula

$$Mg_xCu_{(0.50-x)}Zn_{0.50}Fe_2(C_2O_4)_3 \cdot nH_2O$$

(x=0.00, 0.05, 0.10, 0.15, 0.20, 0.25, 0.30, 0.35, 0.40, 0.45, 0.50) were carried out by manual method in static air atmosphere. The total mass loss % and stepwise mass loss % values are in good agreement with theoretically calculated mass loss % values. The thermal decomposition of oxalate complexes occur at relatively lower temperatures (561 to 698 K). The lowering of decomposition temperatures may be attributed to earlier initiation of Fe^{2+} oxalate in oxalate complexes.

At temperatures between 598–698 K the thermal decomposition of Cu–Mg–Zn–Fe solid solution oxalate complexes leads to formation of ferrites of spinel structure. After tampering at 873 and 1273 K, homogeneous ferrites arise, which is revealed from XRD studies.

Keywords: co-precipitation technique, Cu–Mg–Zn ferrites, decomposition termination temperature, spinel phase

Introduction

Cu–Mg–Zn ferrites are becoming important due to their economy over Ni–Cu–Zn ferrites and their utility in electromagnetic part such as rotary transformer, DY core, EMI core [1]. The methods of preparation of ferrites in general are classified into two groups (i) conventional ceramic methods and (ii) wet chemical methods. The formation of MFe_2O_4 by ceramic method using oxides has several disadvantages such as non-homogeneity, large particle size, low surface area and poor sinterability [2]. Wet chemical methods such as co-precipita-

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tion, hydrothermal oxidation, spray drying, freeze drying can yield fine particles (ferrites) from 10 to 100 nm [3]. The major advantages [4] of these methods are as follows:

(i) Uniform ultrafine particles of high surface area are formed.

(ii) Chemical homogeneity on an atomic scale is achieved by starting with well mixed solutions.

(iii) High chemical purity and strain free materials are obtained as they do not need grinding or ball milling.

(iv) Convenient shape of articles using low temperature casting methods become possible.

(v) They are highly reactive as they are synthesized at such lower temperature.

In view of these advantages, we have synthesized Cu–Mg–Zn ferrites by co-precipitation method using oxalate precursor. Oxalate precursors are usually preferred due to their low solubility, low decomposition temperatures [5]. Besides they yield very fine particle size (100–2000 Å) [5]. Earlier some workers [6, 7] have reported synthesis of Cu–Mg–Zn ferrites by standard ceramic method.

This paper describes thermal studies on solid solution of mixed oxalate complexes synthesized by co-precipitation method.

Experimental

Materials and method

Metal acetates of copper, magnesium, zinc (s.d. Fine, India) AR grade were used as starting materials. Metal acetates are best starting materials as they yield acetic acid as a by-product [8]. Ferrous (Fe^{2+}) acetate was synthesized by dissolving 'Fe' metal powder (Loba Chemie, AR grade) in glacial acetic acid (s.d. Fine, AR grade), in CO_2 atmosphere till it dissolved quantitatively.

The oxalates were prepared by method suggested by Wickham [9]. The calculated amounts of copper acetate, magnesium acetate, zinc acetate were dissolved in doubly distilled water. The solutions of the respective metal acetate thus obtained were heated. The warm metal acetate solutions of Cu^{2+}, Mg^{2+}, Zn^{2+} and above synthesized Fe^{2+} acetate solution (total metal ion concentration=0.45 M) were added dropwise to a 0.60 M oxalic acid solution and stirred vigorously on a magnetic stirrer for one hour digested for 10 min. The yellow crystalline precipitate being filtered through buckner funnel, washed with doubly distilled water and dried at 373 K.

Thermal analysis

A laboratory built thermobalance consisting of a chainomatic balance (K. Roy, Varanashi) of 0.1 mg accuracy, a silica tube furnace, pyrometer (Elec-

troflow, England) of 10 K accuracy maximum up to 1273 K, a temperature controller (Type 8D-1P automatic Electric) and a chromel-alumel thermocouple placed in vicinity of sample (for sensing temperature) was employed in the present work. A heating rate of 3°C min^{-1}, 50–70·10^{-6} kg of sample of 250–200 mesh particle size was used for all the measurements. All measurements were carried out in static air atmosphere from room temperature upto 973 K in a borosil glass cup. The performance of instrument was verified by the TG of $CaC_2O_4 \cdot H_2O$ and $CuSO_4 \cdot 5H_2O$. The temperatures were corrected for thermocouple nonlinearity and procedural decomposition temperatures.

Isothermal mass loss study

Accurately weighed oxalate complex ($1 \cdot 10^{-3}$ kg) was placed in silica crucible in a computer controlled furnace (Carbolite, U.K.) for half an h at temperature 873 K. Hence total mass loss and mass loss % were determined.

X-ray diffraction study (XRD)

The solid solution of co-precipitated oxalate complexes were decomposed in air at their respective decomposition termination temperatures obtained from TG's for three h, at 873 K for one h and at 1273 K for four h. The X-ray diffraction patterns were recorded using Philips X-ray Diffractometer Model PW 1710 using CuK_α radiation (λ=1.5405 A U) in the 2θ range of 20° to 80° and in the intensity range of 200 to 1000 (Fig. 3).

Results and discussion

The mass loss studies of solid solution of mixed oxalate complexes having general formula,

$$Mg_xCu_{(0.50-x)}Zn_{0.50}Fe_2(C_2O_4)_3 \cdot nH_2O$$

prepared by co-precipitation technique were carried out by isothermal mass loss method and thermogravimetric (manual) method to fix nH_2O in each oxalate complex.

The Table 1 includes experimentally observed total mass loss % (by isothermal mass loss and TG manual methods) in comparison with total mass loss % based on theoretical calculations. The Table 1 also presents the proposed formulae for respective oxalate complexes. From the Table 1, it is clearly seen that experimentally observed total mass loss % are in good agreement with theoretically calculated values. Hence the composition of nH_2O in proposed oxalate complex seems to be justified. The proposed formulae for oxalate complex are also in agreement with earlier investigations made by Dollimore *et al.* [10], Dollimore *et al.* [11], Wickham [9] and Langbein *et al.* [12].

Table 1 Mass loss % values obtained by isothermal, TG (manual) method and theoretical calculations and proposed formulae for oxalate complexes

Proposed formulae for oxalate complex	Total mass loss/%		
	isothermal	TG manual	theoretical
$Cu_{0.50}Zn_{0.50}Fe_2(C_2O_4)_3 \cdot 6.5H_2O$	57.40	56.84	56.90
$Mg_{0.05}Cu_{0.45}Zn_{0.50}Fe_2(C_2O_4)_3 \cdot 7.5H_2O$	58.00	57.98	58.45
$Mg_{0.10}Cu_{0.40}Zn_{0.50}Fe_2(C_2O_4)_3 \cdot 7.5H_2O$	58.40	59.62	58.75
$Mg_{0.15}Cu_{0.35}Zn_{0.50}Fe_2(C_2O_4)_3 \cdot 7.5H_2O$	58.40	58.25	58.99
$Mg_{0.20}Cu_{0.30}Zn_{0.50}Fe_2(C_2O_4)_3 \cdot 7.5H_2O$	58.40	57.92	58.64
$Mg_{0.25}Cu_{0.25}Zn_{0.50}Fe_2(C_2O_4)_3 \cdot 6.5H_2O$	56.60	54.39	56.49
$Mg_{0.30}Cu_{0.20}Zn_{0.50}Fe_2(C_2O_4)_3 \cdot 6.5H_2O$	58.20	57.71	58.12
$Mg_{0.35}Cu_{0.15}Zn_{0.50}Fe_2(C_2O_4)_3 \cdot 7.5H_2O$	59.40	58.32	59.67
$Mg_{0.40}Cu_{0.10}Zn_{0.50}Fe_2(C_2O_4)_3 \cdot 7.5H_2O$	59.40	60.27	58.88
$Mg_{0.45}Cu_{0.05}Zn_{0.50}Fe_2(C_2O_4)_3 \cdot 6.5H_2O$	58.80	59.58	58.91
$Mg_{0.50}Zn_{0.50}Fe_2(C_2O_4)_3 \cdot 6.5H_2O$	58.00	58.00	58.00

The curves showing mass loss % *vs.* temperature have been shown in Figs 1–2. The first part of curve corresponds to dehydration step (step I) representing loss of water of crystallization from oxalate complex, whereas second part of curve (step II) corresponds to decomposition of anhydrous oxalate complex (Fig. 1).

Dehydration step

From the curves (Figs 1–2), it is clearly seen that dehydration shows a single step in case of oxalate complex of general composition.

$$Mg_xCu_{(0.50-x)}Zn_{0.50}Fe_2(C_2O_4)_3 \cdot nH_2O$$

where, x=0.00, 0.05, 0.20, 0.30, 0.35 and 0.45.

However, for oxalate complex with x=0.10, 0.15, 0.25, 0.40 and 0.50 (Fig. 2), the step I of dehydration indicates presence of two substeps. The substep I shows partial dehydration of the oxalate complex, whereas substep II shows complete dehydration of respective oxalate complex, thereby giving anhydrous oxalate complex.

Thus in view of this observation it may be expected that anhydrous oxalate complex having general formula,

$$Mg_xCu_{(0.50-x)}Zn_{0.50}Fe_2(C_2O_4)_3$$

may have been formed.

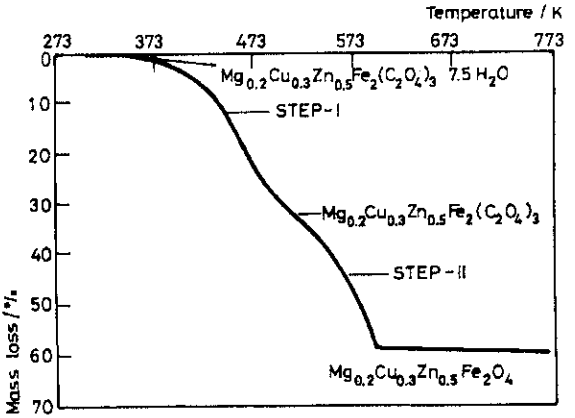

Fig. 1 TG curve of oxalate having composition $Mg_{0.20}Cu_{0.30}Zn_{0.50}Fe_2(C_2O_4)_3 \cdot 7.5H_2O$

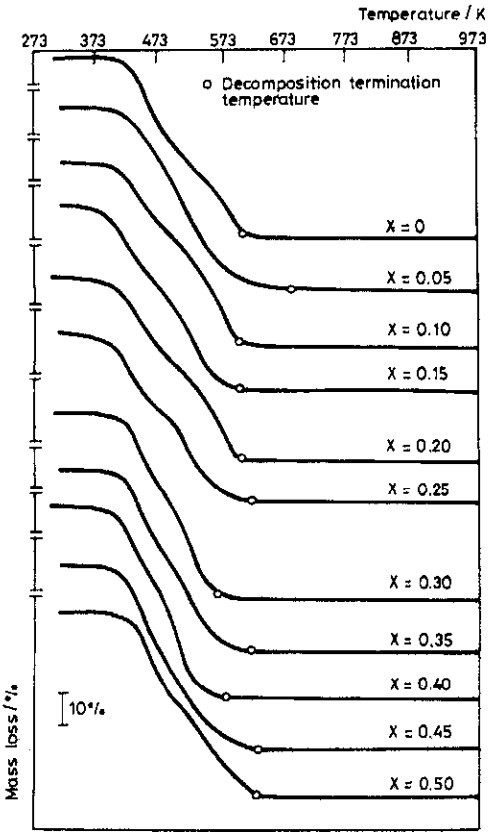

Fig. 2 TG curves of oxalate complexes having general composition $Mg_xCu_{(0.50-x)}Zn_{0.50}Fe_2(C_2O_4)_3 \cdot nH_2O$ (x=0.00, 0.05, 0.10, 0.15, 0.20, 0.25, 0.30, 0.35, 0.40, 0.45, 0.50)

Table 2 Stepwise mass loss % during dehydration and decomposition by TG (manual) method and theoretical calculations

x	Stepwise mass loss/%					
	TG (manual)			Theoretical		
	dehydration	decomposition	total	dehydration	decomposition	total
0.00	21.00	35.84	56.84	21.00	35.90	56.90
0.05	24.10	33.88	57.98	23.56	34.89	58.45
0.10	23.90	35.72	59.62	23.74	35.01	58.75
0.15	24.00	34.25	58.25	23.64	35.35	58.99
0.20	23.90	34.02	57.92	23.80	34.84	58.64
0.25	21.50	32.89	54.39	21.38	35.11	56.49
0.30	21.74	35.97	57.71	21.46	56.66	58.12
0.35	24.00	34.32	58.32	23.68	35.99	59.67
0.40	24.50	35.77	60.27	24.14	34.74	58.88
0.45	21.10	34.40	58.50	24.22	34.69	58.91
0.50	24.00	34.00	58.00	24.00	34.00	58.00

Table 2 summarizes the stepwise mass loss % from TG curves during dehydration as well as decomposition steps and also theoretical mass loss % for the respective oxalate complexes. From Table 2 it is evident that mass loss % observed during dehydration step agrees well with theoretically calculated mass loss % values. This fact further supports the composition of nH_2O in proposed formulae in oxalate complexes.

Decomposition step

The observation of a single step in thermograms of oxalate complexes during decomposition (Figs 1–2) may be taken as an indication of homogeneous phase.

According to Dollimore *et al.* [11] the decomposition of oxalate of the type MC_2O_4 (where M=Zn, Cu, Mg etc.) produce oxides as an end product, when they are decomposed in air as per reaction,

$$MC_2O_4 \rightarrow MO + CO\uparrow + CO_2\uparrow$$

As mass loss % during decomposition agrees well with theoretically calculated mass loss % values assuming mixed oxide as an end product, the decomposition of solid solution of oxalate complex may be represented by general reaction:

$$Mg_xCu_{(0.50-x)}Zn_{0.50}Fe_2(C_2O_4)_3 \rightarrow Mg_xCu_{(0.50-x)}Zn_{0.50}Fe_2O_4 + 4CO\uparrow + 2CO_2\uparrow$$

(anhydrous mixed oxalate complex) (end product - ferrites) (evolved gases)

Table 3 Onset and termination temperatures during dehydration and decomposition steps

	TG (manual)					
	dehydration (step I)/K				decomposition (step II)/	
x	substep I		substep II		K	
	onset	termination	onset	termination	onset	termination
0.00	428	478	–	–	478	603
0.05	398	498	–	–	498	683
0.10	373	423	423	488	488	598
0.15	373	438	438	473	473	698
0.20	348	478	–	–	478	598
0.25	336	426	426	461	461	623
0.30	398	458	–	–	458	561
0.35	373	468	–	–	468	623
0.40	373	436	436	456	456	573
0.45	373	463	–	–	463	623
0.50	361	423	423	456	456	598

Table 3 summarizes onset and termination temperatures during dehydration and decomposition of solid solution of oxalate complexes. From Table 3 it can be seen that oxalate complexes have been dehydrated completely in the range 456 to 498 K, where as most of anhydrous oxalate complexes have been decomposed completely in the range 573 to 623 K, except for oxalate complex with x=0.05, 0.15, 0.30, where decomposition (termination) temperatures are 683, 698 and 561 K respectively. According to Duval [13] single oxalates of Cu^{2+}, Mg^{2+}, Zn^{2+} and Fe^{2+} decompose completely in air medium at temperatures 767, 773, 863 and 468 K respectively. It is interesting to note that solid solution of oxalate complex have been decomposed completely at comparatively lower temperatures than those of individual oxalates of Cu^{2+}, Mg^{2+}, Zn^{2+} and at comparatively higher temperatures than Fe^{2+} oxalate. This fact may be attributed to the formation of homogeneous phase during synthesis of oxalate complex.

It may be assumed that the lowering of decomposition temperatures of solid solution of oxalate complex is caused by earlier initiation of exothermic decomposition of Fe^{2+} oxalate in it, the local heat thus generated being sufficient to effect decomposition of Cu^{2+}, Mg^{2+}, Zn^{2+} oxalates as well. In such a case the onset decomposition temperature of oxalate complex would have been comparable to Fe^{2+} oxalate (Table 4) and the final termination temperature would have been comparable to that of Zn^{2+} oxalate (Table 4). This is contrary to our observation in that, onset decomposition temperatures of all oxalate complexes are higher than individual Fe^{2+} oxalate, and temperatures of completion of decomposition are distinctly lower than that of individual Zn^{2+} oxalate.

Table 4 The thermal data for oxalates of Mg^{2+}, Cu^{2+}, Zn^{2+}, Fe^{2+}

Oxalate	Stable	Dehydration/ K	Stable as anhydrous oxalate	Decompoisition/ K
$MgC_2O_4 \cdot 2H_2O$	453	453–523	523–673	773 → MgO
$CuC_2O_4 \cdot 0.5H_2O$	–	–	373–543	561 (abrupt) 767 → CuO black
$ZnC_2O_4 \cdot 2H_2O$	348	348–438	Unstable	553–863 863 → ZnO
FeC_2O_4	–	–	–	468 (two stages)

These observations seem to indicate that during co-precipitation Fe^{2+}, Mg^{2+}, Zn^{2+} and Cu^{2+} oxalates form an interpenetrating matrix representing in dry state, a metastable solid solution at grain boundaries.

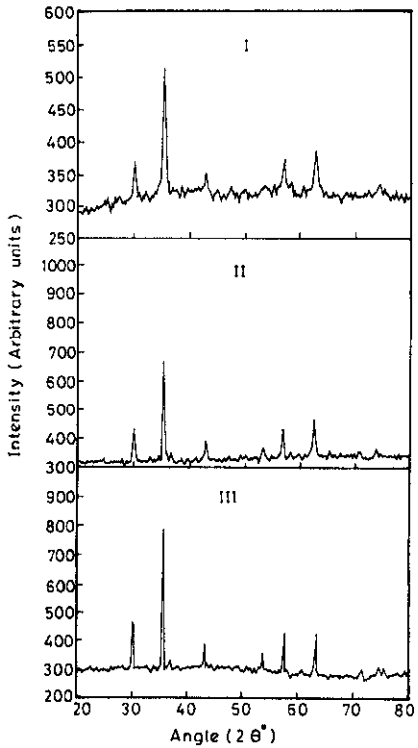

Fig. 3 XRD patterns of (I) oxalate complex decomposed at 598 K for 3 h, (II) decomposed at 873 K for 1 h (III) finally sintered at 1273 K for 4 h in case of ferrite composition with x=0.20

XRD study

From the representative XRD for x=0.20 (Fig. 3), it is clearly seen that after decomposition at 598 K, peaks occurred which are of typical Cu–Mg–Zn ferrite and indicate formation of single spinel phase. With increasing temperature peak intensities grow due to crystallinity increase at simultaneous decrease of half intensity width. X-ray diffractograms do not point out intermediate occurrence of any impurity phase detectable by XRD.

Conclusions

1. Cu–Mg–Zn ferrites are formed by thermal decomposition of homogeneous solid solution oxalate of Cu^{2+}, Mg^{2+}, Zn^{2+} and Fe^{2+}.

2. The formation of ferrite takes place at lower temperatures (561–698 K) than that required for solid state reaction. The decomposition of solid solution oxalates and formation of ferrites occur simultaneously.

3. XRD studies reveal formation of single spinel phase at 598 K for oxalate complex with x=0.20.

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