Thermal study of ferritization temperature of Cu–Mg–Zn ferrites: TG/DTG/DTA (STA) studies

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Abstract

Oxalates of Cu^{2+}, Mg^{2+}, Zn^{2+} and Fe^{2+} were coprecipitated from the mixture of respective acetate solutions using 0.6 M oxalic acid solution to form a homogeneous solid solution $Mg_xCu_{(0.5-x)}Zn_{0.5}Fe_2(C_2O_4)_3 \cdot nH_2O$ with x=0.00, 0.20, 0.25 and 0.40. To determine ferritization (formation of ferrite) temperature of resulting ferrite system, $Mg_xCu_{(0.5-x)}Zn_{0.5}Fe_2O_4$ with x=0.00, 0.20, 0.25 and 0.40, TG/DTG/DTA studies (STA) were carried out on coprecipitated oxalate complexes. These studies revealed the low ferritization temperature ($326°$–$370°C$) of the ferrite system and occurrence of simultaneous decomposition and ferritization processes. The ferrite system was characterized using X-ray diffraction study, which revealed the presence of single spinel phase. © 1998 Elsevier Science B.V.

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1. Introduction

High performance ferrites are commonly produced by a solid-state reaction using intimately mixed fine powders of component oxides and other salts to increase reactivity of component oxides [1]. To obtain an end product having a single phase, it is essential to maintain scrupulous reaction conditions. Besides these commonly employed conventional methods, various nonconventional methods also have been

investigated and evaluated [2–4]. Schuele [5] has synthesized copper ferrite having fine particle size by suitably heat treating coprecipitated oxalates of the Cu–Fe system. Wickham [6] has synthesized spinel ferrites MFe_2O_4 (where M=Mg^{2+}, Mn^{2+}, Zn^{2+}, Ni^{2+}, Co^{2+}) by decomposing mixed metal oxalate complexes, wherein ignition temperature ranges from $1000°$ to $1310°C$, depending on respective M. Moreover, Langbein et al. [7] and St. Fischer et al. [8] have separately synthesized nickel–zinc ferrites by thermal decomposition of coprecipitated oxalates. Bremer et al. [9] have investigated preparation of manganese–zinc ferrites by thermal decomposition of solid solution of oxalate complexes.

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Synthesis of Cu–Mg–Zn ferrites using a solid solution of component oxides have been reported by Koh et al. [10,11] and Hak et al. [12]. However, synthesis of Cu–Mg–Zn ferrites by nonconventional methods (using organic precursors) have not been reported so far. The present paper reports our nonconventional method which has an advantage of obtaining homogeneous solid solution of respective oxalates. On further decomposition, it results in the desired ferrite system. It also includes TG/DTG/DTA study (STA) for detection of its ferritization temperature and X-ray diffraction study for characterization of the resultant ferrite system.

2. Experimental

Bremer et al. [9] have prepared manganese-zinc ferrites by modifying the Wickham method [6] for preparation of individual oxalates. The method has an advantage over the conventional metal oxide process in which acetic acid is obtained as an important by-product resulting from the synthesis of oxalates using respective metal acetates [13].

In the present case, iron (II) acetate was prepared by adding glacial acetic acid (slightly in excess) to the required quantity of AR grade iron metal powder. To avoid the oxidation of iron (II) to iron (III), the reaction was carried out in CO_2 atmosphere instead of N_2 atmosphere employed in the above mentioned method [9]. To maintain the desired stoichiometry, the required quantities of copper acetate, zinc acetate, magnesium acetate, iron (II) acetate prepared as above (having total metal iron concentration=0.45 M) were added dropwise to the 0.6 M oxalic acid solution to precipitate the required oxalate complex. The oxalic acid solution was continuously stirred for homogeneous mixing. The yellow crystalline precipitate was digested for 10 min and allowed to cool to room temperature. The supernatant liquid/solution was filtered off. The precipitate was washed with doubly distilled water and dried in an oven at 100°C.

2.1. Thermal analysis: TG/DTG/DTA study (STA)

Simultaneous thermal analysis (STA) of mixed oxalate complexes was carried out using Netzsch STA 409 differential thermal analyzer. The samples were heated in air at a heating rate of 10°C min^{-1} TG, DTG, DTA curves were recorded simultaneously in the temperature range from room temperature to 700°C.

### 2.2. X-ray diffraction (XRD) study

The solid solution of coprecipitated oxalate complexes were decomposed at their respective ferritization temperature obtained from TG's for three hours and 600°C for one hour in air. X-ray diffraction (XRD) patterns were recorded using Philips X-ray diffractometer model PW 1710 using CuK_α radiation (λ=1.5405 Å) in the 20<2θ<80° range and in the intensity range from 250 to 1000 counts (Fig. 4).

Using standard conversion table, 'd' values for the corresponding '2θ' were derived. The lattice parameter were computed using these d values and the respective (h,k,l) parameters, which identified that the samples are single spinel ferrites. The reported lattice-parameter value for $Mg_{0.5}Zn_{0.5}Fe_2O_4$ is 0.840 nm [14] and for $Cu_{0.5}Zn_{0.5}Fe_2O_4$ it is 0.841 nm [15]; these values have been compared with the experimental data to characterize the samples.

3. Results and discussion

3.1. TG/DTG/DTA study (STA)

On analyzing the TG/DTG/DTA experimental data, thermal decomposition of a solid solution of an oxalate complex is observed to take place in two distinct steps: Step I includes dehydration of the oxalate complex and Step II – decomposition of anhydrous oxalate complex (Fig. 1) for the composition with x=0.00 of the oxalate complex represented by the formula:

$$Mg_xCu_{(0.5-x)}Zn_{0.5}Fe_2(C_2O_4)_3 \cdot nH_2O$$
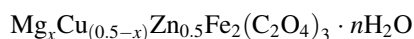
For the composition with x=0.25, however, Step I indicates the presence of two substeps as seen from the DTG/DTA curves (Fig. 2). All the DTA curves show that dehydration is an endothermic reaction represented by a sharp peak, whereas decomposition in air is an exothermic reaction indicated with a broad
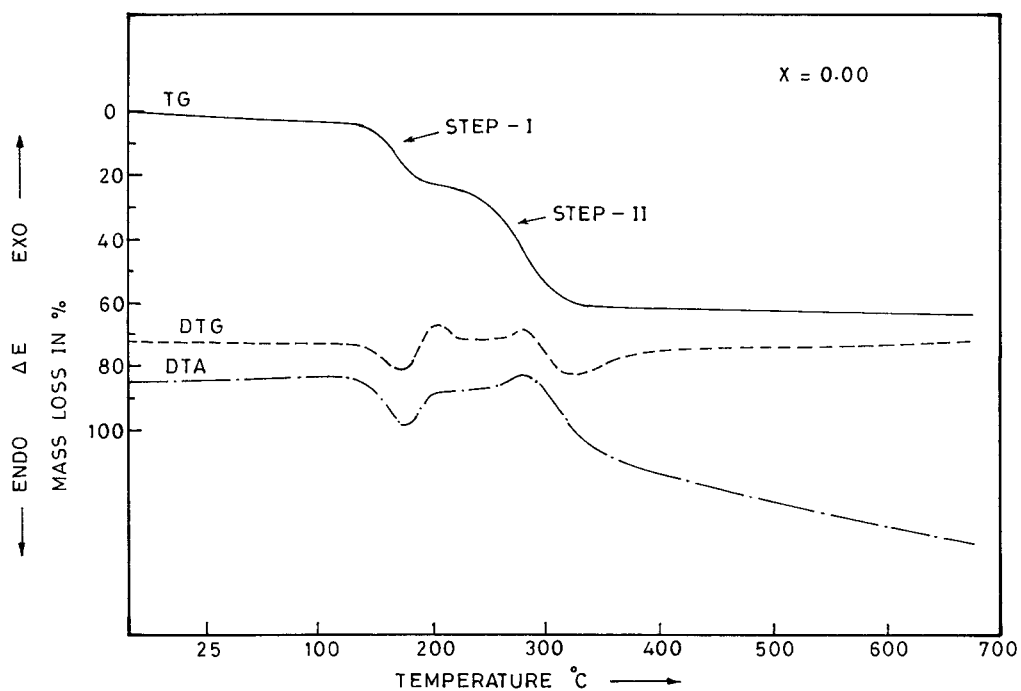
Fig. 1. STA of oxalate complex: $Cu_{0.5}Zn_{0.5}Fe_2(C_2O_4)_3$, 6.5 H_2O.
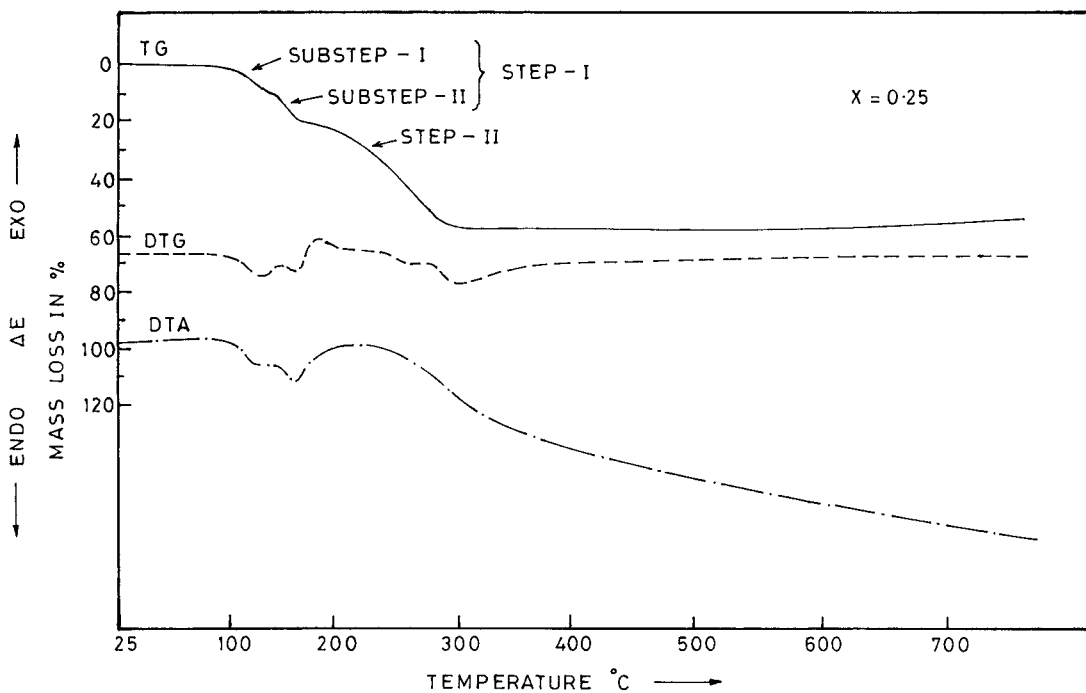
Fig. 2. STA of oxalate complex: $Mg_{0.25}Cu_{0.25}Zn_{0.50}Fe_2(C_2O_4)_3 \times \cdot 6.5H_2O$.
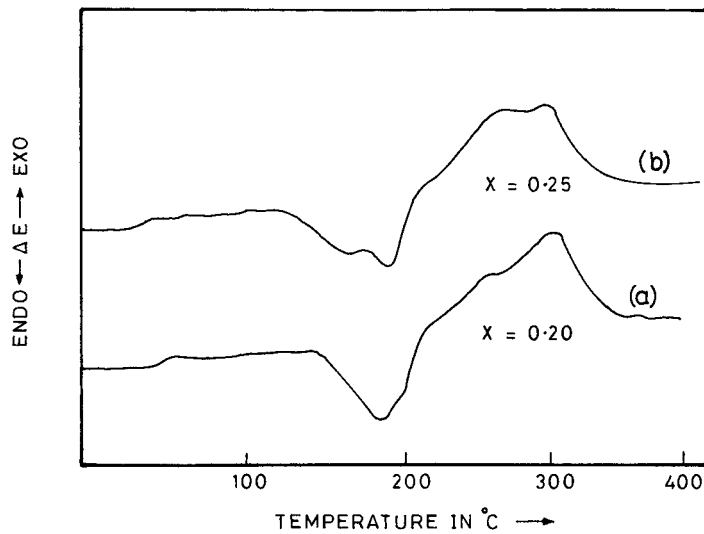
Fig. 3. DTA of oxalate complex: (a) $Mg_{0.20}Cu_{0.30}Zn_{0.50}Fe_2(C_2O_4)_3 \cdot 7.5H_2O$; and (b) $Mg_{0.25}Cu_{0.25}Zn_{0.50}Fe_2(C_2O_4)_3 \cdot 6.5H_2O$.

Table 1
Stepwise and total mass loss in % and its variation with x for the oxalate complex system: $Mg_xCu_{(0.5-x)}Zn_{0.5}Fe_2(C_2O_4)_3 \cdot nH_2O$

| x | Proposed formulae for oxalate complexes | Stepwise and total mass loss in % | | | | | |
| | | TG (experimental) | | | TG (theoretical) | | |
		dehydration	decomposition	total	dehydration	decomposition	total
0.00	$Cu_{0.5}Mg_{0.5}Zn_{0.5}Fe_2(C_2O_4)_3 \cdot 6.5H_2O$	20.40	37.23	57.63	21.00	35.90	56.90
0.20	$Mg_{0.20}Cu_{0.30}Zn_{0.50}Fe_2(C_2O_4)_3 \cdot 7.5H_2O$	19.80	39.22	59.02	23.80	34.82	58.62
0.25	$Mg_{0.25}Cu_{0.25}Zn_{0.50}Fe_2(C_2O_4)_3 \cdot 6.5H_2O$	20.65	35.87	56.52	20.70	35.79	56.49
0.40	$Mg_{0.40}Cu_{0.10}Zn_{0.50}Fe_2(C_2O_4)_3 \cdot 7.5H_2O$	21.96	37.37	59.33	24.14	35.53	59.67

Table 2
Onset and termination temperatures observed during dehydration and decomposition steps for $Mg_xCu_{(0.5-x)}Zn_{0.5}Fe_2(C_2O_4)_3 \cdot nH_2O$ system with various x

| x | TG dehydration (Step I)/(°C) | | | | decomposition (Step II)/(°C) | |
| | substep I | | substep II | | onset | termination |
	onset	termination	onset	termination		
0.00	116	204	—	—	204	326
0.20	116	209	—	—	209	337
0.25	148	185	185	209	209	337
0.40	142	191	191	209	209	370

hump (Figs. 1 and 2). The exothermic reaction of decomposition is confirmed by separately recording DTA's (Fig. 3) for the samples with compositions x=0.20 and 0.25.
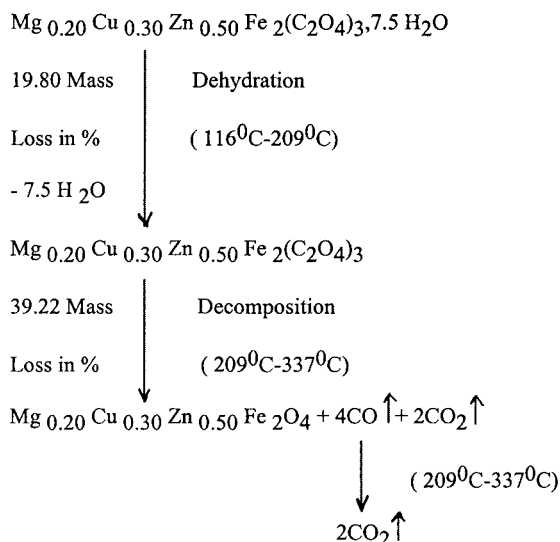
Table 1 includes experimentally observed total mass loss in %, in comparison with total mass loss in % based on theoretical calculations. Table 1 also presents the proposed formulae for respective oxalate complexes. The total mass loss in % experimentally observed is used to calculate the total number of water molecules present in the respective oxalate complex system and agrees well with the corresponding theoretically calculated one. Table 1 also gives stepwise mass loss in % observed experimentally from TG curves during the dehydration and decomposition steps as compared with theoretical ones. The corresponding onset and termination temperature for these steps observed from TG/DTG/DTA curves are given in Table 2. These temperatures observed for separately recorded DTA curves remain the same. DTA curves also indicate the type of reaction occurring in these temperature ranges (Figs. 1–3).

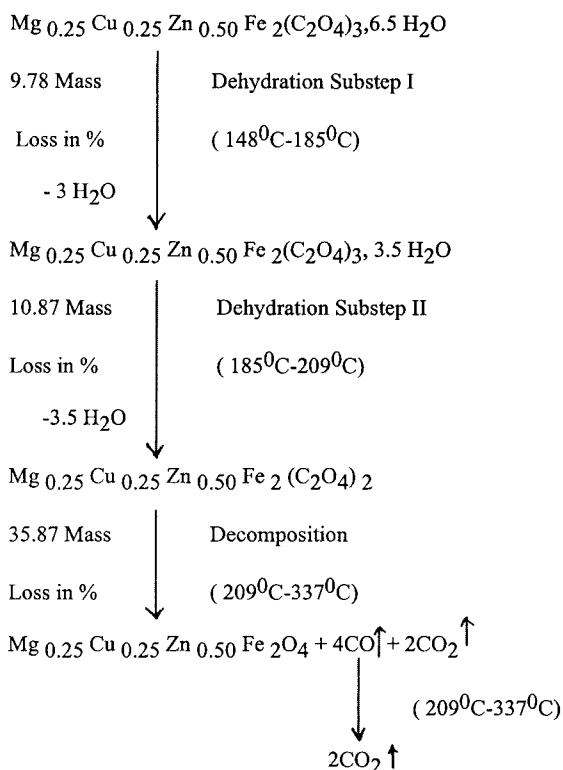The dehydration and decomposition steps/reactions can be represented as follows,

(1) $x = 0.00$

$Cu_{0.5} Zn_{0.5} Fe_2(C_2O_4)_3, 6.5H_2O$

20.40 Mass | Dehydration
Loss in % | (116^0C-204^0C)
- 6.5 H_2O

$Cu_{0.5} Zn_{0.5} Fe_2(C_2O_4)_3$

37.23 Mass | Decomposition
Loss in % | (204^0C-326^0C)

$Cu_{0.5} Zn_{0.5} Fe_2O_4 + 4CO\uparrow + 2CO_2\uparrow$

(204^0C-326^0C)

$2CO_2\uparrow$

(2) $x = 0.20$

$Mg_{0.20} Cu_{0.30} Zn_{0.50} Fe_2(C_2O_4)_3, 7.5 H_2O$

19.80 Mass | Dehydration
Loss in % | (116^0C-209^0C)
- 7.5 H_2O

$Mg_{0.20} Cu_{0.30} Zn_{0.50} Fe_2(C_2O_4)_3$

39.22 Mass | Decomposition
Loss in % | (209^0C-337^0C)

$Mg_{0.20} Cu_{0.30} Zn_{0.50} Fe_2O_4 + 4CO\uparrow + 2CO_2\uparrow$

(209^0C-337^0C)

$2CO_2\uparrow$

(3) $x = 0.25$

$Mg_{0.25} Cu_{0.25} Zn_{0.50} Fe_2(C_2O_4)_3, 6.5 H_2O$

9.78 Mass | Dehydration Substep I
Loss in % | (148^0C-185^0C)
- 3 H_2O

$Mg_{0.25} Cu_{0.25} Zn_{0.50} Fe_2(C_2O_4)_3, 3.5 H_2O$

10.87 Mass | Dehydration Substep II
Loss in % | (185^0C-209^0C)
-3.5 H_2O

$Mg_{0.25} Cu_{0.25} Zn_{0.50} Fe_2 (C_2O_4)_2$

35.87 Mass | Decomposition
Loss in % | (209^0C-337^0C)

$Mg_{0.25} Cu_{0.25} Zn_{0.50} Fe_2O_4 + 4CO\uparrow + 2CO_2\uparrow$

(209^0C-337^0C)

$2CO_2\uparrow$

(4)　　x = 0.40

$Mg_{0.40}Cu_{0.10}Zn_{0.50}Fe_2(C_2O_4)_3, 7.5 H_2O$

10.50 Mass	Dehydration Substep I
Loss in %	
$- 3.5 H_2O$	(142^0C-191^0C)

$Mg_{0.40}Cu_{0.10}Zn_{0.50}Fe_2(C_2O_4)_3, 4 H_2O$

11.46 Mass	Dehydration Substep II
Loss in %	(191^0C-209^0C)
$- 4 H_2O$	

$Mg_{0.40}Cu_{0.10}Zn_{0.50}Fe_2(C_2O_4)_3$

| 37.37 Mass | Decomposition |
| Loss in % | (209^0C-370^0C) |

$Mg_{0.40}Cu_{0.10}Zn_{0.50}Fe_2O_4 + 4CO\uparrow + 2CO_2\uparrow$

　　　　　　　　　　　　　(209^0C-370^0C)

$2CO_2\uparrow$

Fig. 4. XRD patterns of oxalate complex with x=0.25: (a) decomposed at 337°C for 3 h; and (b) decomposed at 600°C for 1 h.
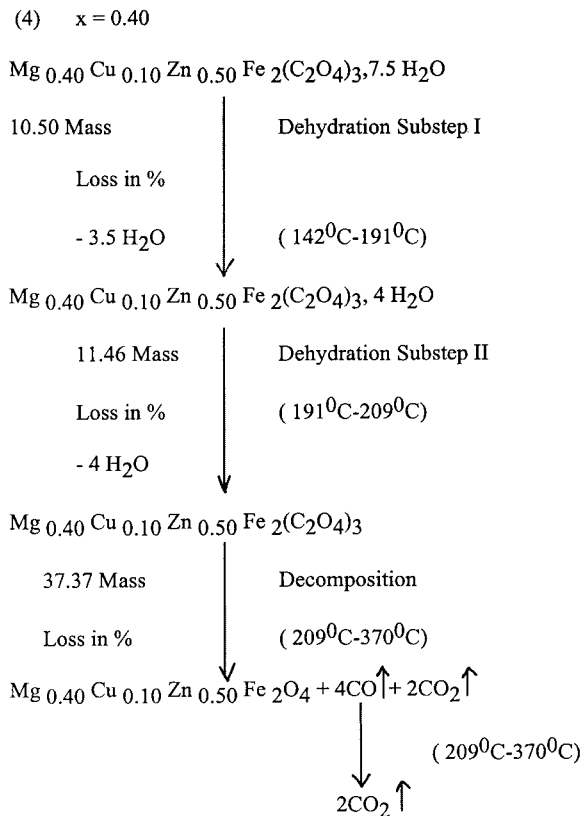
The ferritization (formation of the ferrite) and decomposition processes are occurring simultaneously in the temperature range of 209° to 370°C (max) as the nascent MO's are highly reactive and, therefore, helps ferritization at a low temperature range, such as 326–370°C. This phenomena has been confirmed by the separate preparation of these compositions at respective ferritization temperatures by following the same procedure, and the ferrites thus formed are characterized by XRD. That any further change is absent is evident from the TG, DTG, DTA curves recorded beyond this temperature range.

3.2. X-ray diffraction (XRD) study

The single spinel phase of all the samples has been characterized by using XRD data from which lattice-parameter constants could be calculated by the standard method.
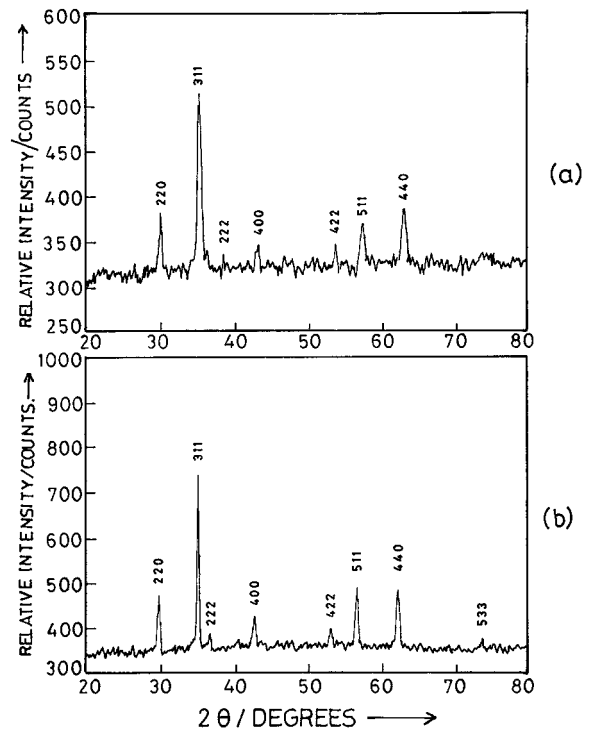
Typical representative XRD patterns for X=0.25 are shown in Fig. 4 in which the oxalate complexes are decomposed at 337°C (ferritization temperature) for 3 h and at 600°C for 1 h. They exhibit a single spinel phase. No other impurity phases existed. The observed lattice parameters are given in Table 3. These values are comparable with those reported [14,15].

The temperature ranges, for the different steps observed during dehydration and decomposition process for each separate oxalate system represented by

Table 3
Variation of lattice parameter, a with x in $Mg_xCu_{(0.5-x)}Zn_{0.5}Fe_2O_4$

Mg^{2+} content x	Lattice parameter, $a\pm0.002$ Å
0.00	8.398
0.20	8.397
0.25	8.386
0.40	8.375

$MC_2O_4 \cdot nH_2O$ (where $M=Mg^{2+}$, Zn^{2+}, Cu^{2+}, Fe^{2+}) have been reported by Duval [16].The maximum temperature required is 590°C in case of decomposition of zinc oxalate to zinc oxide, among the required metal oxalates. Therefore, to make sure that dehydration and decomposition reactions are complete, we have synthesized ferrite system at 600°C and recorded their XRD pattern. For characterization of the samples, a similar procedure has been adopted. On comparing all the XRD patterns, it revealed that ferritization is completed at such a low temperature, ranging from 326° to 370°C, for compositions with $x=0.00$, 0.20, 0.25, 0.40 in $Mg_xCu_{(0.5-x)}Zn_{0.5}Fe_2O_4$.

4. Conclusions

1. Pure Cu–Mg–Zn ferrites are formed by direct thermal decomposition of Cu^{2+}–Mg^{2+}–Zn^{2+}–Fe^{2+} oxalate complexes (solid solution).
2. Ferritization occurs at a temperature (i.e. in the 326–370°C range), depending on the stoichiometry. The ferritization temperature is far lower than that required for conventional solid-state reaction. Such a low temperature of ferritization leads to the production of these ferrites at a very low cost.
3. Decomposition and ferritization take place simultaneously.
4. XRD studies revealed the formation of single spinel phase at 337° and 600°C.

The magnetic properties of all these samples have been reported elsewhere [17].

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