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REACTIVITY OF BINARY MIXTURES OF Cu(II) OXALATE AND La(III) OXALATE

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Abstract

Reactivity of binary mixtures of oxalates of Cu(II) and La(III) was studied by observing their thermal behaviours in decomposition using TG, DTA and XRD techniques to set the temperature conditions for preparations of various composites of oxides of Cu(II) and La(III). In the thermal behaviour it was found that the decomposition of Cu(II) oxalate is not affected while that of La(III) oxalate is drastically affected in the case of all the mixtures. The decomposition temperature at which La(III) oxide is formed is lowered by 250 K in the case of all the mixtures while the complete decomposition occurred at ~723 K only in the case of mixtures containing excess Cu(II) oxalate.

At ~823 K La_2CuO_4 phase is developed in all the mixtures while α-La and Cu_2La phases are also detected in mixtures containing excess Cu(II) oxalate. Therefore, the temperature 823 K was found to be suitable to prepare various composites viz. La_2CuO_4, $La_2CuO_4{\cdot}La_2O_3$ and $La_2CuO_4{\cdot}CuO$ to study their electrical properties.

Keywords: La_2CuO_4, oxalates, TG-DTA, XRD

Introduction

In order to prepare composites of oxides of Cu(II) and La(III) by decomposing mixtures of oxalates of corresponding metal ions, at elevated temperatures the knowledge of thermal behaviours and thereby reactivity of both the oxalates in mixtures is essential.

The decomposition of La(III) oxalate starts at ~653 K and La(III) oxide is formed around 953 K [1–6]. Cu(II) oxalate undergoes a strongly exothermic decomposition reaction at ~553 K yielding Cu(I) oxide which is oxidized to Cu(II) oxide on further heating in oxygen [7, 8]. In the earlier work [8] on thermal behaviour of mixtures prepared by physical mixing of Cu(II) oxalate with oxalate of Fe(II), Co(II) or Ni(II) it is reported that all the four oxalates exhibit the same thermal behaviours in the decomposition in oxygen up to 743 K as those observed in the cases of individual oxalates. As the organic parts in all the above mentioned oxalates decompose in strongly exothermic processes in the temperature range of 503 to 603 K it is difficult to trace the exact effect of heat evolved in exothermic reactions on decomposition of components in mixtures.

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If mixtures of oxalates of Cu(II) and La(III) are subjected to thermal decomposition it will be interesting to observe thermal behaviours and thereby reactivity of both the oxalates in binary mixtures at different stages of heating as regards the following aspects:

(A) Effect of heat evolved in the exothermic decomposition of Cu(II) oxalate on the decomposition of La(III) oxalate: As the heat will be transferred to particles of La(III) oxalate the decomposition temperatures of the latter will be shifted towards lower temperature side and the effect will be pronounced in the case of mixtures containing excess Cu(II) oxalate and,

(B) The homogeneous mixtures of oxides of Cu(II) and La(III) existing in highly dispersed form will be produced at the end of complete decomposition of both the oxalates and there is a probability of development of the phase La_2CuO_4 at temperature around 953 K. Hence, there is no necessity of firing and grinding of oxides repeatedly at elevated temperatures greater than 1273 K [9–14] to produce the phase La_2CuO_4, a superconducting composite oxide.

The temperatures at which the complete decomposition occurs and the phase La_2CuO_4 develops will be fixed in the case of each mixture from the observed thermal behaviours of oxalates to prepare composites to study their electrical properties.

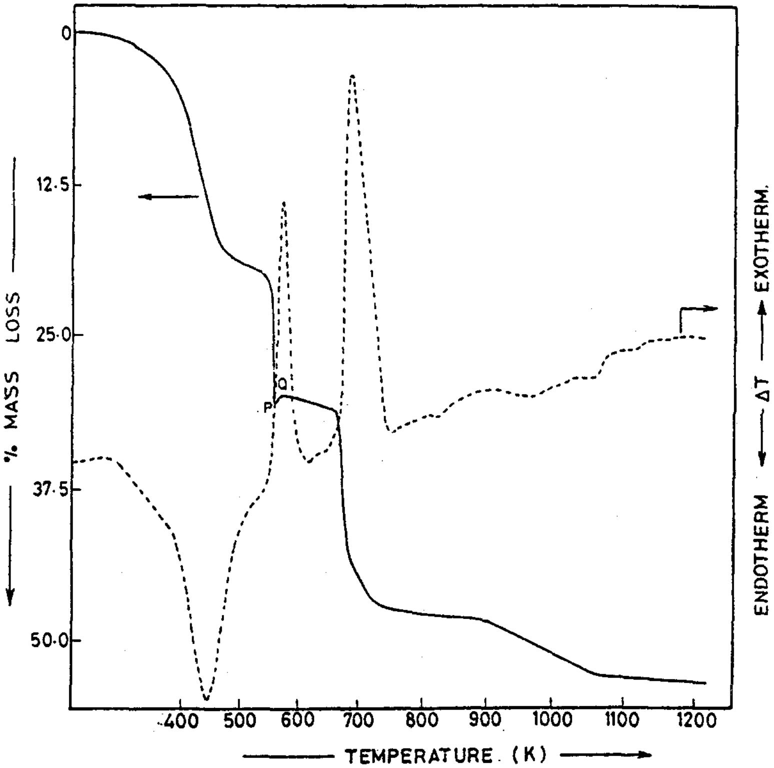

Fig. 1 TG and DTA traces of 1:1 mm sample

Experimental

Pure crystalline trihydrate Cu(II) oxalate and La(III) oxalate containing different water molecules were prepared adopting methods reported earlier [1, 15] and their mixtures by mechanical mixing (mm). Mixtures in 1:1, 2;1 and 3.5:1 mole proportions were prepared by adding appropriate quantities of Cu(II) oxalate and La(III) oxalate (baked at 393 K for 5 h) in agate mortar. While mixing the oxalates, it was verified that one mole of La(III) oxalate is coordinated with 7 moles of H_2O in 1:1 and 2:1 mm samples while one mole of H_2O in 3.5:1 mm sample. Therefore, 1:1 mm contains total 10 moles of H_2O while 2:1 and 3.5:1 mm samples contain 13 and 11.5 total moles of H_2O respectively.

All the chemicals used were of 'Analar' grade and purity of oxalates was checked by chemical analysis.

TG and DTA

TG and DTA traces were simultaneously recorded at the heating rate 10 K min^{-1} in the temperature range of 298 to 1273 K for all the mixtures separately on

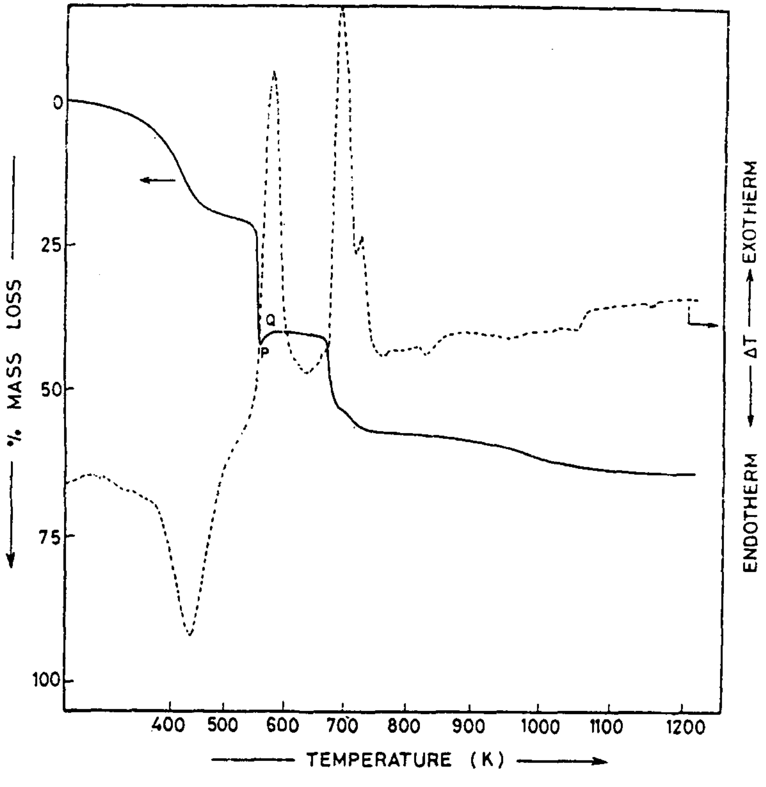

Fig. 2 TG and DTA traces of 2:1 mm sample

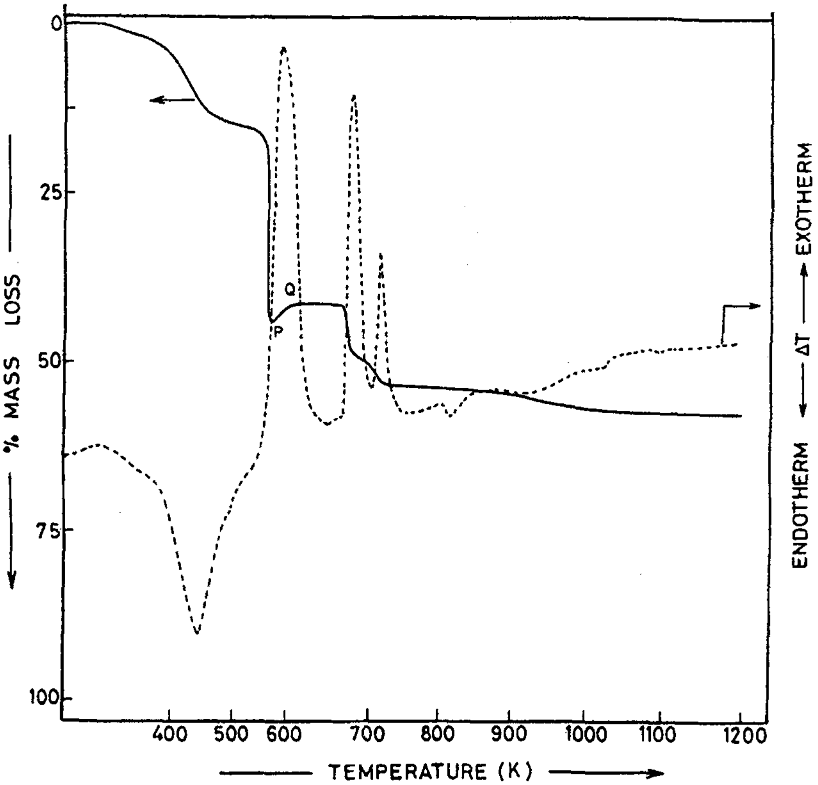

Fig. 3 TG and DTA traces of 3.5:1 mm sample

MOM Derivatograph, OD type 102 under following experimental conditions: (1) mass of sample ~200 mg, (ii) α-Al_2O_3 as reference sample, (iii) dry air atmosphere, (iv) sample holder made of platinum crucibles and (v) thermocouple made from platinum and platinum rhodium alloy wires. Results are shown in Figs 1–3 and tabulated in Table 1.

XRD studies

Mixtures were heated at the rate 10 K min^{-1} upto 573, 723, 823 or 1173 K (designated as 5 Ht, 7 Ht, 8 Ht or 11 Ht respectively) and cooled to room temperature in dry air and their XRD patterns were recorded on Rigaku PR-511 at 2000 Hz using Cu target and are shown in Figs 4–8.

Results and discussion

At the end of Step I, all the mixtures are completely dehydrated and in step II, the complete decomposition of Cu(II) oxalate and partial decomposition of La(III) oxalate take place as follows [1, 2, 7 and 8] (Figs 1–3 and Table 1):

$$2CuC_2O_{4(s)} + O_{2(g)} \xrightarrow{\text{exothermic}} 2CuO_{(s)} + 4CO_{2(g)} \tag{1}$$

$$La_2(C_2O_4)_{3(s)} \xrightarrow{\text{exothermic}} 2Int'_{(s)} + CO_{(g)} \tag{2}$$

$$La_2(C_2O_4)_{3(s)} \xrightarrow{\text{exothermic}} Int''_{(s)} + 2CO_{(g)} \tag{3}$$

$$2La_2(C_2O_4)_{3(s)} \xrightarrow{\text{exothermic}} 2Int'''_{(s)} + 5CO_{(g)} \tag{4}$$

where Int′, Int″ and Int‴ are the intermediate species formed in reactions (2), (3) and (4) occurred in 1:1, 2:1 and 3.5:1 mm samples respectively.

The amount of heat generated in the decomposition Cu(II) oxalate to Cu(II) oxide (reaction (1)) is transferred to the particles of La(III) oxalate in the mixture and the latter, instead of ~653 K [1, 2] starts its decomposition to organic part at ~563 K producing temperature shift of ~80 K towards lower temperature side.

XRD patterns of all the mixtures – 5 Ht samples (Fig. 4a, b, c) show lines of weak intensities of CuO phase. Therefore, it appears that although at ~573 K the complete decomposition of Cu(II) oxalate to Cu(II) oxide takes place the latter is not fully crystallized.

In step (III), all the intermediate species Int′, Int″ and Int‴ formed in reactions (2), (3) and (4) respectively, further decompose to La(III) oxy carbonate and then partially decompose to La(III) oxide as follows:

$$2Int'_{(s)} \xrightarrow{\text{exothermic}} La_2O_2CO_{3(s)} + 2CO_{2(g)} + 2CO_{(g)} \tag{5}$$

$$La_2(C_2O_4)_{3(s)} \xrightarrow{\text{exothermic}} 2Intt_{(s)} + 2CO_{(g)} + CO_{2(g)} \tag{6}$$

$$La_2O_2CO_{3(s)} \xrightarrow{\text{exothermic}} La_2O_{3(s)} + CO_{2(g)} \tag{7}$$

where ‘Intt’ is an intermediate species formed in reaction (6)

$$Int''_{(s)} \xrightarrow{\text{exothermic}} La_2O_2CO_{3(s)} + 2CO_{2(g)} + CO_{(g)} \tag{8}$$

$$2Int'''_{(s)} \xrightarrow{\text{exothermic}} 2La_2O_2CO_{3(s)} + 4CO_{2(g)} + CO_{(g)} \tag{9}$$

In the step IV, Intt (reaction (6)) ultimately decomposes to 0.5 moles of La_2O_3 in the following reaction:

$$2Intt_{(s)} \rightarrow La_2O_{3(s)} + 2CO_{2(g)} + CO_{(g)} \tag{10}$$

XRD patterns of all mm – 7 Ht samples (Fig. 5a,b,c) show lines of major phases of CuO, $La_2O_2CO_3$ and La_2O_3 while in addition to them, lines of high intensity of La_2CuO_4 phase along with Cu_2O phase appear only in XRD pattern of 3.5:1 mm – 7 Ht sample (Fig. 5c). La(III) oxide and Cu(II) oxide react at temperatures above 1273 K to produce La(III) cuprate while in the present work, the phase of La_2CuO_4 is developed in the following reaction [9, 10, 13, 14, 16] at ~823 K:

$$CuO_{(s)} + La_2O_{3(s)} \xrightarrow{\text{endothermic}} La_2CuO_{4(s)} \tag{11}$$

Table 1 Thermal analysis data of decomposition of various binary mixtures of oxalates of Cu(II) and La(III)

Composition of mixture	TG					DTA		Reactions correlated
Mole proportion $CuC_2O_4{\cdot}3H_2O$ $+La_2(C_2O_4)_3{\cdot}nH_2O$	Step	Mass loss/%		Loss and uptake of species moles	Composition at step end, moles	Endo-peak/	Exo-peak/	
	T/K	Obs.	Theor.			K		
1:1 for $n=7$	Step I 298–533	20.34	20.618	$-10H_2O$	anhydrous CuC_2O_4 $La_2(C_2O_4)_3$	~443		dehydration
	Step II 543–568	9.884	9.847	$-2CO_2$ $-0.5CO$ $+0.5O_2$	CuO Int′ 0.5La2(C_2O_4)		~573	(1) and (2) for 0.5 moles
	Step III 568–733	16.28	16.488	$-2CO_2$ $-2CO$	CuO Intt $0.5La_2O_3$		~683	(5) and (7) both for 0.5 moles of $La_2O_2CO_3$ and (6) for 0.5 moles of $La_2(C_2O_4)_3$ and (12) to (14)
	Step IV 733–1223	6.64	6.641	$-CO_2$ $-0.5CO$	CuO La_2O_3	~753 ~813		$CuLaO_3$ phase (11)
		Total 53.144	Total 53.594			~968		(10)
	Step V 1223–1273	1.1628				~1063 ~1243		(15) α–La phase

Table 1 Continued

Composition of mixture	TG					DTA		Reactions correlated
Mole proportion $CuC_2O_4 \cdot 3H_2O$ $+La_2(C_2O_4)_3 \cdot nH_2O$	Step *T*/K	Mass loss/% Obs.	Mass loss/% Theor.	Loss and uptake of species moles	Composition at step end, moles	Endo-peak/ K	Exo-peak/ K	
2:1 for $n=7$	Step I 298–533	21.21	21.61	$-13H_2O$	anhydrous $2CuC_2O_4$ $La_2(C_2O_4)_3$	~423		dehydration
	Step II 543–583	18.48	18.4682	$-4CO_2$ $-2CO$ $+O_2$	2CuO Int″		~573	(1) and (3)
	Step III 583–688	13.03	12.74	$-2.5CO_2$ $-CO$	2CuO $0.5La_2O_2CO_3$ $0.5La_2O_3$		~693	(8)
	Step IV 688–743	2.424	2.0315	$-0.5CO_2$	2CuO La_2O_3	~763 ~833	~723	(7) for 0.5 moles (12), (13) and (14) $CuLaO_3$ phase (11)
		Total 55.144	Total 54.85			~963		(15)
	Step V 743–1223	6.0605				~1053 ~1153		α–La phase Cu_2La phase

Table 1 Continued

Composition of mixture Mole proportion $CuC_2O_4 \cdot 3H_2O$ $+La_2(C_2O_4)_3 \cdot nH_2O$	TG					DTA		Reactions correlated
	Step T/K	Mass loss/% Obs.	 Theor.	Loss and uptake of species moles	Composition at step end, moles	Endo-peak/ K	Exo-peak/ K	
3.5:1 for $n=1$	Step I 298–533	16.66	16.468	$-11.5H_2O$	anhydrous $3.5CuC_2O_4$ $La_2(C_2O_4)_3$	~423		dehydration
	Step II 533–578	24.975	24.91	$-7CO_2$ $-2.5CO$ $+1.75O_2$	3.5CuO Int″		~573	(1) and (4) for one mole
	Step III 578–703	9.592	9.5947	$2.5CO_2$ 0.5CO	3.5CuO $0.5La_2O_2CO_3$ $0.5La_2O_3$		~678	(9) for one mole of Int‴
							~723	(7) for 0.5 mole (12), (13) and (14)
	Step IV 703–713	1.7	1.7024	$0.5CO_2$	3.5CuO La_2O_3	~763 ~813 ~923		$CuLaO_3$ phase (11) (15)
		Total 52.927	Total 52.675					
	Step V 713–1273	5.55				~1023 ~1093		α–La phase Cu_2La phase

where loss (–) and uptake (+)

Carbon monoxide generated in reactions (1) and (9) in steps I to IV in the case of all the mixtures, partially reacts with oxygen from air and the remaining with Cu(II) oxide as follows [17]:

$$2CO_{(g)} + O_{2(g)} \xrightarrow{\text{exothermic}} 2CO_{2(g)} \tag{12}$$

$$2CuO_{(s)} + CO_{(g)} \xrightarrow{\text{exothermic}} Cu_2O_{(s)} + CO_{2(g)} \tag{13}$$

$$Cu_2O_{(s)} + CO_{(g)} \xrightarrow{\text{exothermic}} 2Cu_{(s)} + CO_{2(g)} \tag{14}$$

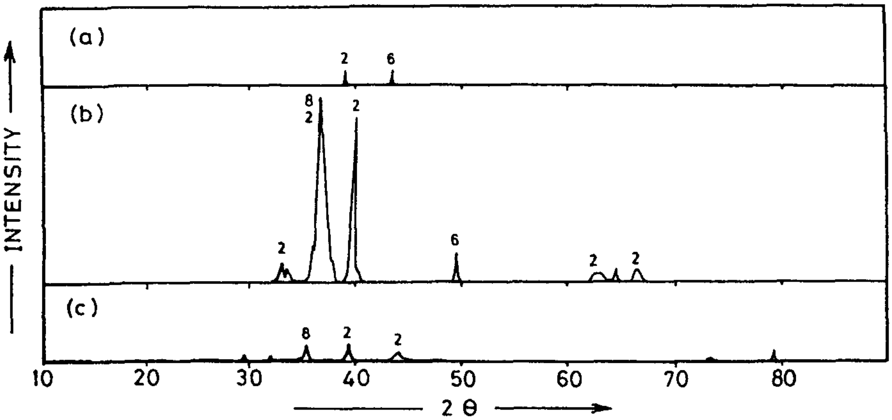

Fig. 4 XRD patterns of (a) 1:1 mm – 5 Ht, (b) 2:1 mm – 5 Ht and (c) 3.5:1 mm – 5 Ht samples

XRD pattern of 1:1 mm – 8 Ht sample shows lines of major phases of La_2CuO_4 and CuO and minor phases of Cu_2O and Cu (Fig. 6a) while that of 2:1 mm – 8 Ht displays lines of major phases of CuO, Cu_2O, La_2O_3 and minor phases of α-La and Cu_2La (Fig. 6b) and that of 3.5:1 mm – 8 Ht shows lines of major phases of La_2CuO_4, La_2O_3, CuO, Cu_2O and Cu and minor phases of α-La and Cu_2La (Fig. 6c).

If one mole of CuO reacts with 0.5 moles of La_2O_3 and 0.25 moles of O_2 $CuLaO_3$ phase [18] will be developed at ~753 K (an endothermic reaction) and in further heating get destroyed and hence not appearing in XRD–8 Ht samples.

The endo-peaks at ~753 and 813 K observed in DTA traces of all the mixtures (Figs 1–3) are correlated with the phases $CuLaO_3$ and La_2CuO_4 (reaction (11)) respectively (Table 1).

It is expected that in the case of 1:1 mm sample the residue at the end of TG at ~1273 K will contain only La(III) cuprate phase on the contrary XRD pattern of 1:1 mm – 11 Ht samples exhibits lines of La_2CuO_4, CuO, La_2O_3 and α-La phases (Fig. 7a).

XRD pattern of 2:1 mm – 11 Ht sample (Fig. 7b) shows lines of predominant phases La_2CuO_4, Cu_2La along with minor phases of CuO, Cu_2O and La_2O_3 while that of 3.5:1 mm – 11 Ht sample displays lines of major phases La_2CuO_4, CuO and

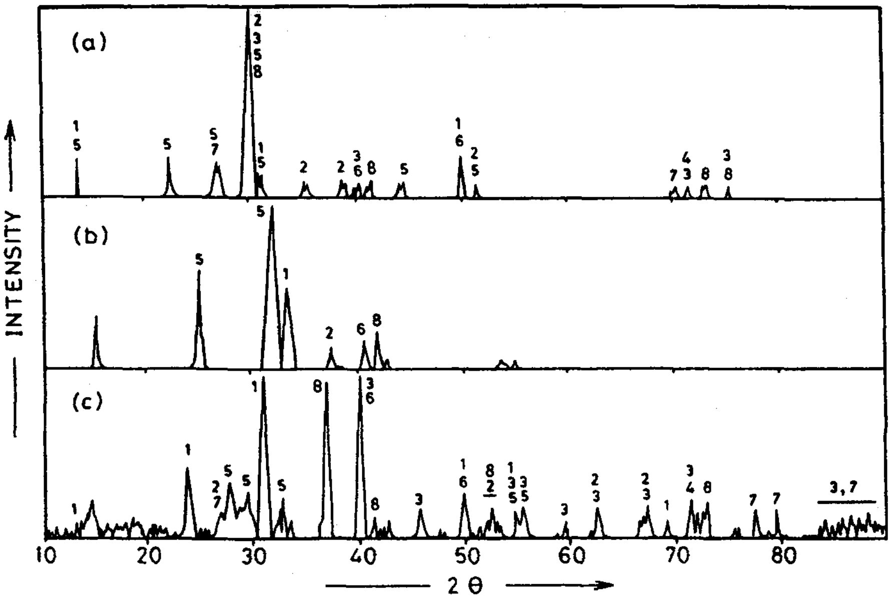

Fig. 5 XRD patterns of (a) 1:1 mm – 7 Ht, (b) 2:1 mm – 7 Ht and (c) 3.5:1 mm – 7 Ht samples

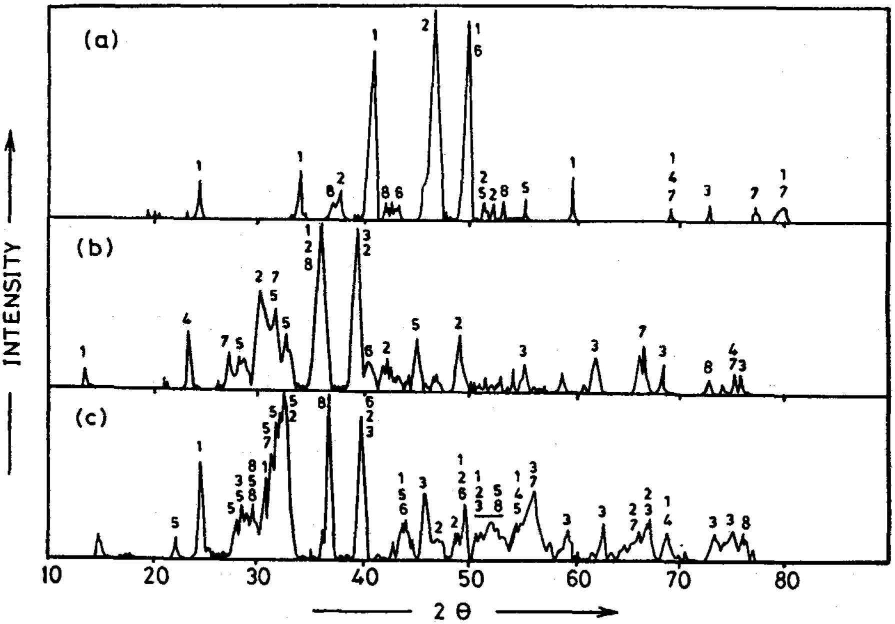

Fig. 6 XRD patterns of (a) 1:1 mm – 8 Ht, (b) 2:1 mm – 8 Ht and (c) 3.5:1 mm – 8 Ht samples

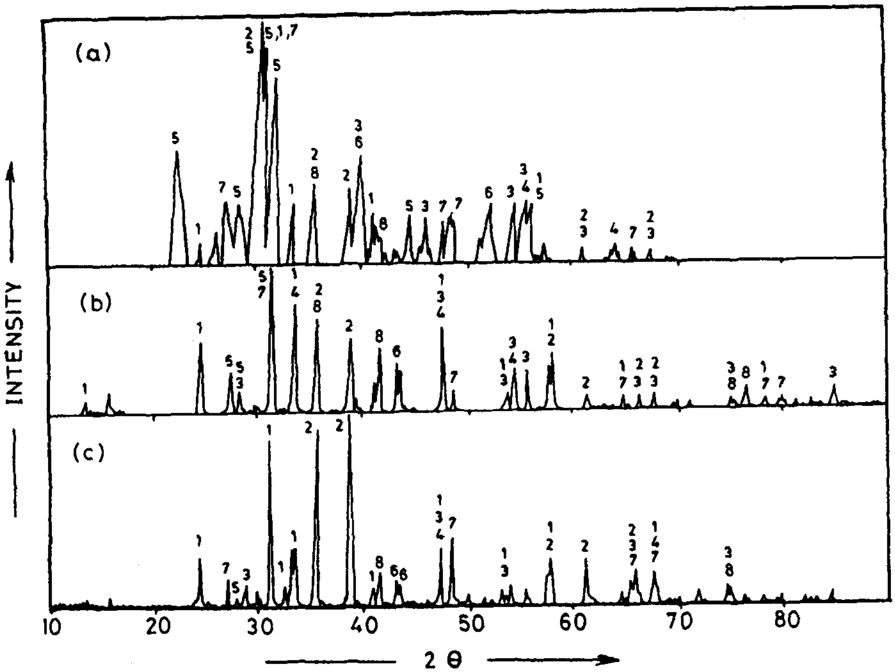

Fig. 7 XRD patterns of (a) 1:1 mm – 11 Ht, (b) 2:1 mm – 11 Ht and (c) 3.5:1 mm – 11 Ht samples

those of minor phases, La_2O_3, α-La and Cu_2O (Fig. 7c). Figure 7 shows lines of $La_2O_2CO_3$ phase which is developed due to the reaction of La(III) oxide with carbon dioxide present in the sample cell, during cooling from 1273 K to room temperature [19]. It was verified by keeping pure La(III) oxide in the atmosphere of carbon dioxide and recording XRD patterns of La(III) oxide before and after the exposure to carbon dioxide (Fig. 8).

Earlier investigators [3–6] have reported that the residues at the TG end of La(III) oxalate and rare-earth oxalates contain some residual carbon mass and the following reaction has been predicted [20]:

$$2CO_{(g)} \rightleftharpoons C_{(g)} + CO_{2(g)} \qquad (15)$$

Considering all the results shown in Figs 1–8 and tabulated in Table 1, the reactivity of oxalates of Cu(II) and La(III) in mixtures, under the present experimental set up is discussed below:

(A) Reactivity with respect to the decomposition of oxalate:

The decomposition of Cu(II) oxalate is unaffected [8] while that of La(III) oxalate is drastically affected in mixtures.

(i) In the case of all the mixtures, the temperature at which individual La(III) oxalate decomposes to organic part is shifted by ~80 K towards lower temperature side i.e. from 653 to 563 K.

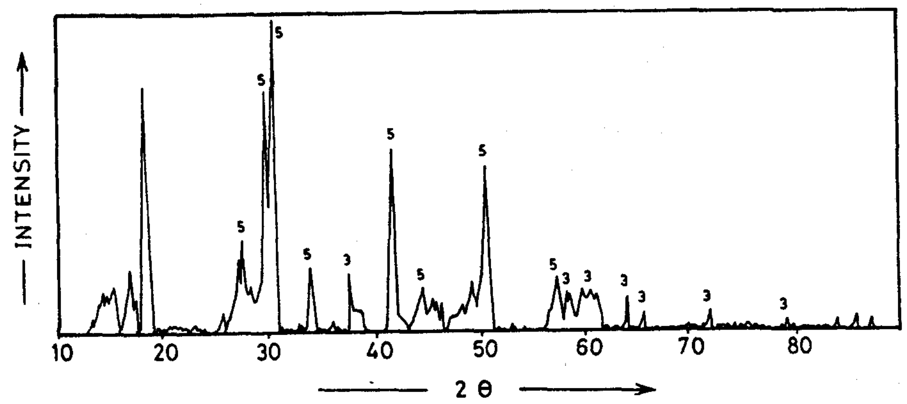

Fig. 8 XRD pattern of La_2O_3 – 11 Ht sample, after the exposure to carbon dioxide

(ii) In the Step II from ~543 to 573 K one mole of La(III) oxalate decomposes to 0.5 moles, 2 and 2.5 moles of CO in 1:1 and 2:1 and 3.5:1 mm samples respectively, hence, higher the quantity of Cu(II) oxalate present in the mixture more the amount of carbon monoxide evolved.

(iii) The temperature at which La(III) oxide forms in the decomposition of individual La(III) oxalate is shifted by ~250 K towards lower temperature side i.e. from 953 to 693 K.

(B) Reactivity with respect to the formation of composites of La_2CuO_4, La_2O_3 and CuO phases.

Only 3.5:1 mm sample provides, (i) composite of La_2CuO_4, La_2O_3 and CuO phases with trace impurity phase of metal La at 823 K and (ii) another composite of La_2CuO_4 and CuO phases with trace impurity phases of Cu_2O and α-La at 1223 K and

(C) Reactivity with respect to the formation of phases of α-La and Cu_2La.

2:1 mm shows highest reactivity with respect to the formation of α-La and Cu_2La phases

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