Journal of Thermal Analysis, Vol. 48 (1997) 819-834

REACTIVITY OF OXALATES OF La(III), Ba(II) AND Cu(II) IN TERNARY MIXTURES

L. Bapat[*], *G. N. Natu*[**], *M. Bhide*[*] *and J. Kher*[*]

[*]Department of Chemistry, N. Wadia College, PUNE 411 001
[**]Department of Chemistry, University of Poona, PUNE, India

Abstract

Composites of cuprates of La(III) and Ba(II) were obtained by decomposing mixtures of oxalates of La(III), Ba(II) and Cu(II) prepared in 1:1:1 and 1:2:3 mol proportions respectively and sintering the oxide products at 1173 K. Reactions studied by TG, DTA and XRD techniques revealed the following features: (i) Decomposition of oxalates of La(III) and Ba(II) is drastically affected in mixtures. Decomposition temperature of organic part in the former (1:1:1) is shifted by ~100 K while that of $BaCO_3$ in the case of latter (1:2:3) is shifted by ~400 K towards lower temperature side. (ii) All exothermic peaks on DTA traces of both the mixtures are allotted to the decomposition of oxalates to Cu_2O, $La_2O_2CO_3$ and $BaCO_3$ phases while endothermic peaks around 863 and 1083 K are assigned for $BaCuO_2$ and La_2CuO_4 phases respectively in the case of former (1:1:1) and endothermic peaks at about 1068, 1136 and 1213 K are correlated with $BaCuO_2$, a composite of La_2O_3, La_2CuO_4 and $La_{0.5}Ba_{0.5}CuO_{3-\delta}$ ($\delta \to 0.5$) phases and $LaBa_2Cu_3O_{7-\delta}$ ($\delta \to 0$) phase respectively in the case of latter (1:2:3) and (iii) Lines of all cuprate compounds appear in XRD patterns of those samples preheated at temperatures ≥873 K. The following reaction is proposed in the case of 1:2:3 mixture:

$$2La_{0.5}Ba_{0.5}Cu^{II}O_{3-\delta}\ (\delta \to 0.5)\ +\ BaCuO_2 \longrightarrow LaBa_2Cu_3O_{7-\delta}\ (\delta \to 0)$$

Keywords: composites of cuprates, DTA, mixture of oxalates, TG, XRD.

Introduction

Various composites of ceramic oxides are prepared either by mixing the corresponding neat oxides in appropriate proportions and firing and sintering them at elevated temperatures or by decomposing the mixtures of nitrates, carbonates, formates, citrates or oxalates of the corresponding cations, prepared in required proportions and sintering the oxide products at high temperatures >1273 [1, 2].

Metal oxalates decompose to either metal or metal oxide or carbonate at different temperatures [3]. Cu(II) oxalate around 553 K decomposes to Cu_2O which is subsequently oxidized to CuO in air [4, 5], La(III) oxalate decomposes to La_2O_3 at ~923 K [6–11] while Ba(II) oxalate decomposes to $BaCO_3$ at ~768 K and further to BaO and BaO_2 around 1273 K [12–14].

In the binary mixtures of CuO and La_2O_3 or CuO and BaO_2 at temperatures >1273 K CuO reacts with La_2O_3 or BaO_2 and produces La_2CuO_4 or $BaCuO_2$ phases respectively [15–17].

0368–4466/97/ $ 5.00

John Wiley & Sons Limited
Chichester

In their work [18–21] on the synthesis of $LaCuO_3$ based $La_{1-x}Ba_xCuO_{3-\delta}$ phases using ternary mixtures of La_2O_3, BaO_2 and CuO it is observed that (i) small amount of BaO is incorporated in La_2CuO_4 to form $La_{2-x}Ba_xCuO_4$ phase and (ii) in excess of Ba(II) the development of La_2CuO_4 phase is supressed and another phase $La_{1-x}Ba_xCuO_{3-\delta}$ is produced [19].

Rao *et al.* [22] in their earlier work on synthesis of $LaBa_2Cu_3O_{7-\delta}$ phase possessing superconducting properties very similar to those of $YBa_2Cu_3O_{7-\delta}$ [23] have shown that with the increase in amount of BaO_2 and CuO in the ternary mixture of La_2O_3, BaO_2 and CuO such as a mixture of oxides in 1:2:3 mol proportion, a single phase of $LaBa_2Cu_3O_{7-\delta}$ can be produced with small impurities of $BaCuO_2$.

Brown *et al.* [5] in their work on thermal analysis of some mixed metal oxalates viz.:Cu(II) oxalate and oxalate of Fe(II) or Co(II) or Ni(II) it is observed that results obtained on ground physical mixtures are the same as those on individual oxalate while results on coprecipitated metal oxalates show a remarkable change in thermal behaviour as observed:

(i) The absence of big exothermic peak on DSC trace which is a characteristic behaviour of Cu(II) oxalate,

(ii) the shifts in decomposition temperatures of oxalates and,

(iii) the evolution of CO and CO_2 gases in various proportions depending upon the surrounding atmosphere, during the heating programme of the co-precipitates.

In the present work, attempts have been made to prepare composites of cuprate compounds by decomposing various ternary mixtures of oxalates of La(III), Ba(II) and Cu(II) and to study the different intermediate phases produced in the progress of reactions adopting TG, DTA and XRD techniques. In the exothermic decomposition of Cu(II) oxalate in air a large amount of heat is generated [4, 5] and it is expected that this heat will be utilized to weaken the bonds in oxalates of La(III) and Ba(II) so that their decompositions will take place at lower temperatures <653 and 773 K respectively [6–11, 14]. The composite prepared in this way will be of superconducting cuprates La_2CuO_4 and $LaBa_2Cu_3O_{7-\delta}$ [22, 23] and metallic conductor $La_{1-x}Ba_xCuO_{3-\delta}$ [18, 20, 21].

Experimental

Ternary mixtures of oxalates of La(III), Ba(II) and Cu(II) were prepared adopting following procedure:

(i) Appropriate quantities of aqueous solutions of $pH=4$, of chlorides of La(III) and Ba(II), required to prepare coprecipitates of their oxalates in 1:1 or 1:2 mol proportions respectively, were added simultaneously to the aqueous solution of sodium oxalate slowly with constant stirring and coprecipitates formed were allowed to settle for the period of 12 h and baked at 393 K for 5 h [6, 12].

(ii) Pure monohydrate of Cu(II) oxalate was prepared adopting method reported earlier [24] and

(iii) Appropriate quantities of co-precipitates (cp) of oxalates of La(III) and Ba(II) and that of Cu(II) oxalate, required to prepare ternary mixtures in 1:1:1 and

1:2:3 mol proportions, respectively, were mechanically mixed in agate morter. The final compositions of mixtures were obtained as follows:

(La(III) oxalate: Ba(II) oxalate)·$4H_2O$+Cu(II) oxalate·H_2O=[(1:1) cp:1]
physical mixture and

(La(III) oxalate: 2Ba(II) oxalate)·$7H_2O$+3Cu(II) oxalate ·H_2O=[(1:2)cp:3]
physical mixture

and hereafter will be described as 1:1:1 and 1:2:3 mm′ respectively.

All the chemicals used were of 'Analar' grade and purity of all the oxalates and the composition of coprecipitates were checked by chemical analysis. Cu(II) oxalate was in crystalline phase while coprecipitates were in amorphous state as checked in their XRD patterns.

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 both of the mixtures on MOM Derivatograph, OD Type 102 under following experimental conditions: (i) mass of sample ~200 mg, (ii) α-Al_2O_3 as a reference sample, (iii) dry air as a furnace atmosphere, (iv) sample holder made up of platinum crucibles and (v) Pt–Pt. Rh thermocouples. Results are shown in Figs 1 and 2.

XRD studies

It was observed that in DTA traces of mixtures, various phases were produced at reaction temperatures 553, 573, 673, 683, 748, 773, 813, 816, 863, 933, 1038, 1068, 1083, 1136 and 1213 K and therefore XRD patterns of those phases were recorded during the progress of reactions as follows:

Several samples of both the mixtures were heated at the rate 10 K min^{-1} up to 593, 693, 873, 1013, 1113, 1163, 1173 or 1253 K (designated as 5 Ht, 6 Ht, 8 Ht, 10 Ht, 11 Ht, 116 Ht, 117 Ht or 125 Ht respectively) and immediately cooled to room temperature within 10 min, in dry air and their XRD patterns were recorded on Rigaku PR-511 using Cu target, K_α line, which are shown in Figs 3 and 4.

Results and discussion

Figure 1 shows TG traces of variation in percentage mass loss against temperature of 1:1:1 and 1:2:3 mm′ samples. In both the cases decomposition takes place in various steps. In the case of former after the dehydration, decomposition starts around 473 K and the continuous mass loss occurs upto 563 K which is followed by the mass gain of 1.635% upto 578 K (at point P). In the case of latter exactly similar variation in percentage mass loss and gain (at point Q) is observed upto ~533 and 553 K respectively. After points P and Q there is continuous mass loss upto 1273 K in both the cases.

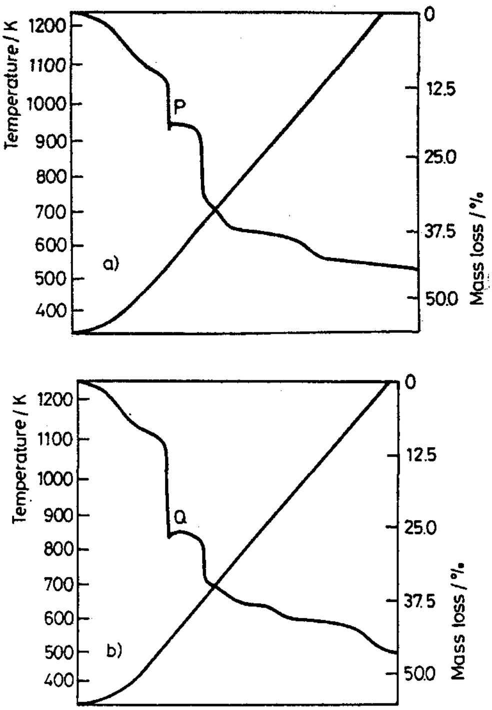

Fig. 1 TG traces of a) 1:1:1 and b) 1:2:3 mm′ samples

Figure 2 shows DTA traces of 1:1:1 and 1:2:3 mm′ samples. In the case of former there are four exothermic (exo-) peaks around 573, 683, 748 and 813 K and four endothermic (endo-) peaks at ~463, 863, 1038 and 1083 K while in the case of latter, there exists three exo-peaks around 553, 673 and 773 K and six endo-peaks at ~373, 816, 933, 1068, 1136 and 1213 K.

In the case of 1:1:1 mm′ sample (Figs 1, 2 and 3 and Table 1): In the step I from 313 to 473 K 8.84% mass loss corresponds to the loss of $5H_2O$ species in the following endothermic reactions [4–7]:

$$(La_2(C_2O_4)_3{\cdot}BaC_2O_4){\cdot}4H_2O(s) \xrightarrow{\text{endothermic}} La_2(C_2O_4)_3{\cdot}BaC_2O_4(s) + 4\,H_2O(g) \qquad (1)$$

$$\text{and, } CuC_2O_4{\cdot}H_2O(s) \xrightarrow{\text{endothermic}} CuC_2O_4(s) + H_2O(g) \qquad (2)$$

The endo-peak around 463 K observed on DTA trace of 1:1:1 mm′ (Fig. 2 and Table 1) is assigned for reactions (1) and (2).

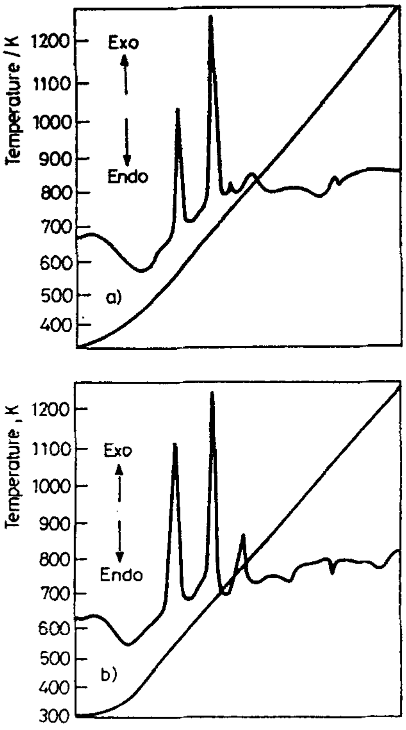

Fig. 2 DTA traces of a) 1:1:1 and b) 1:2:3 mm′ samples

In the step II from 473 to 578 K (Fig. 1) 10.67% mass loss corresponds to the loss of $2CO_2$, CO and uptake of $0.25O_2$ species which are accounted in the following exothermic reactions [4–7]:

$$4CuC_2O_4(s) + O_2(g) \xrightarrow{\text{exothermic}} 2Cu_2O(s) + 8CO_2(g) \tag{3}$$

$$\text{and, } La_2(C_2O_4)_3(s) \xrightarrow{\text{exothermic}} Int'(s) + CO(g) \tag{4}$$

where, Int′=intermediate species formed in the decomposition of La(III) oxalate and starting with one mol of Cu(II) oxalate $0.5Cu_2O$ will be produced. The mass gain is observed at point P on the TG trace of 1:1:1 mm′ sample (Fig. 1).

In the case of single components La(III) oxalate [6, 7] and Ba(II) oxalate [12, 13] organic part starts decomposing around 653 and 768 K respectively and therefore CO gas evolved in step II is considered to be one of the decomposition products of La(III) oxalate only (reaction (4)). The amount of heat generated in the reaction (3) is transferred on oxalates of La(III) and Ba(II) and the former instead of decomposing at ~653 K starts its decomposition around 520 K in step II and hence the observed temperature shift, $\Delta T \approx 100$ K towards lower temperature side (Table 1).

The exo-peak at ~573 K recorded on DTA trace of 1:1:1 mm′ sample (Fig. 2 and Table 1) is correlated with reactions (3) and (4).

In the step III from 578 to 683 K (Fig. 1 and Table 1) ~13.41% mass loss corresponds to the loss of $2CO_2$ and 2CO and mass gain of $0.25O_2$ species in the following exothermic reactions [4–7, 12, 13]:

$$2Cu_2O(s) + O_2(g) \xrightarrow{\text{exothermic}} 4CuO(s) \tag{5}$$

$$\text{Int}'(s) \xrightarrow{\text{exothermic}} \text{Int}''(s) + 2CO_2(g) + CO(g) \tag{6}$$

$$\text{and, } BaC_2O_4(s) \xrightarrow{\text{exothermic}} BaCO_3(s) + CO(g) \tag{7}$$

where Int′ and Int″ = intermediate species formed in the decomposition of La(III) oxalate in reactions (4) and (6) respectively and starting with $0.5Cu_2O$, CuO is obtained in reaction (5).

It is proposed that amount of heat evolved in reactions (5) and (6) and in oxidation of carbon monoxide to carbon dioxide in air is transferred on Ba(II) oxalate resulting in its decomposition to $BaCO_3$ in reaction (7) around 630 K and hence the observed decomposition temperature shift of $\Delta T \approx 100$ K towards lower temperature side [12].

The exo-peak around 683 K traced in DTA is assigned for reactions (5) and (6) (Fig. 2 and Table 1).

In the step IV, from 683 to 963 K (Fig. 1 and Table 1) ~7.31% mass loss corresponds to the loss of CO and CO_2 species in the following reactions:

$$\text{Int}''(s) \xrightarrow{\text{exothermic}} La_2O_2CO_3(s) + CO(g) \tag{8}$$

$$\text{and, } BaCO_3(s) \xrightarrow{\text{endothermic}} BaO(s) + CO_2(g) \tag{9}$$

where Int″ = intermediate species formed in reaction (6).

BaO as soon as formed in the reaction (9) reacts with CuO and develops new phase $BaCuO_2$ [17, 25] as follows:

$$BaO + CuO \xrightarrow{\text{endothermic}} BaCuO_2(s) \tag{10}$$

In the case of mixture containing $BaCO_3$ and other oxides, BaO forms at high temperature >1273 [14] while in the present sample, it forms at ~873 K and hence the observed temperature shift of $\Delta T \approx 400$ K towards lower temperature side.

The exo-peaks around 748 and 813 K are correlated with reactions (7) and (8) respectively while the endo peak around 863 K is assigned for the reactions (9) and (10) (Fig. 2 and Table 1).

The XRD pattern of 1:1:1 mm′ – 8 Ht sample (Fig. 3a) shows lines of major phases $BaCuO_2$ and $La_2O_2CO_3$ which are consistent with the proposed reactions (5) to (10).

Table 1 Thermal analysis data of deompositions of 1:1:1 and 1:2:3 mm′ samples

	TG				DTA			
Composition of mixture, mol proportion	T_{step}/K	Mass loss/% obs.	calc.	Loss and uptake of species	Composition at step end	Endo-peak/K	Exo-peak/K	Reactions correlated
$(La_2(C_2O_4)_3 \cdot BaC_2O_4) \cdot$ $4H_2O + CuC_2O_4 \cdot H_2O$ [1:1:1 mm′]	Step I 313 to 473	8.84	8.89	$-5H_2O$	$La_2(C_2O_4)_3$. BaC_2O_4, CuC_2O_4 (mol)	~463		(1) and (2)
	Step II 473 to 578	10.67	10.67	$-2CO_2$ $-CO$ $+0.25O_2$	Int′ BaC_2O_4 $0.5Cu_2O$		~573	(3) and (4)
	Step III 578 to 683	13.41	13.44	$-2CO_2$ $-2CO$ $+0.25O_2$	Int″ $BaCO_3$ CuO		~683	(5) for 0.5 mol and (6)
	Step IV 683 to 963	7.31	7.109	$-CO$	$La_2O_2CO_3$		~748	(7)
				$-CO_2$	BaO		~813	(8)
					CuO	~863		(9) and (10)
	Step V 963 to 1133	4.57	4.35	$-CO_2$	La_2O_3	~1038		(11)
					BaO	~1083		(12)
					CuO			
		Total 44.80	Total 44.46					

Table 1 Continued

Composition of mixture, mol proportion	TG				DTA			
	T_{step}/K	Mass loss/%		Loss and uptake of species	Composition at step end	Endo-peak/K	Exo-peak/K	Reactions correlated
		obs.	calc.					
$(La_2(C_2O_4)_3 \cdot 2BaC_2O_4) \cdot$ $7H_2O + 3CuC_2O_4 \cdot H_2O$ [1:2:3 mm']	Step I 313 to 513	10.26	11.03	$-10H_2O$	$La_2(C_2O_4)_3 \cdot$ $2BaC_2O_4$, ~373 $3CuC_2O_4$		(13), (2)	for 3 mol
	Step II 513 to 553	14.535	14.71	$-6CO_2$ $+0.75O_2$	$La_2(C_2O_4)_3$ $2BaC_2O_4$ $1.5Cu_2O$		~553	(3) for 3 mol
	Step III 553 to 653	1.7	1.71	$-CO$	Int′ $2BaC_2O_4$ $1.5Cu_2O$			
	Step IV 653 to 668	6.84	7.09	$-2CO_2$ $-CO$	Int″ $2BaC_2O_4$ 3CuO[5]		~673	(5) for 1.5 mol and (6)
	Step V 668 to 793	3.55	3.42	$-2CO$	Int″ $2BaCO_3$ 3CuO		~773	(7) for 2 mol and (8)

Table 1 Continued

Composition of mixture, mol proportion	TG T_{step}/K	Mass loss/% obs.	 calc.	Loss and uptake of species	DTA Composition at step end	Endo-peak/K	Exo-peak/K	Reactions correlated
	Step VI			$-CO$	$La_2O_2CO_3$	~816		(14)
	793 to 1093	3.56	3.42	$-0.5CO_2$	$1.5BaCO_3$	~933		(9)
								for 0.5 mol
					$0.5BaCuO_2$	~1068		(10)
					$2.5CuO$			for 0.5 mol
	Step VII				$0.45BaCO_3$	~1136		(11), (12) and (15)
	1093 to 1273	5.32	5.38	$-2CO_2$	$0.05BaO_2$	~1213		(16)
					$0.5BaCuO_2$			(9) and (17)
					$0.5La_2CuO_4$			for 0.05 mol
					$2La_{0.5}Ba_{0.5}CuO_{3-\delta}$			
					$(\delta \rightarrow 0.5)$			
		Total	Total					
		45.765	45.765					

where (–) = loss and (+) = uptake

In the step V from 963 to 1133 K (Fig. 1 and Table 1) ~4.57% mass loss corresponds to the loss of CO_2 species in the following endothermic reaction:

$$La_2O_2CO_3(s) \xrightarrow{\text{endothermic}} La_2O_3(s) + CO_2(g) \qquad (11)$$

The endo-peak around 1038 K observed on DTA trace of 1:1:1 mm′ sample is allotted to the reaction (11) (Fig. 2 and Table 1).

Almost all the amount of CuO is consumed in reaction (10) to form $BaCuO_2$ and very small amount will react with La_2O_3 to produce La_2CuO_4 phase [15, 25, 26] as follows:

$$La_2O_3 + CuO \xrightarrow{\text{endothermic}} La_2CuO_4(s) \qquad (12)$$

The small endo-peak around 1083 traced in DTA of 1:1:1 mm′ is assigned for the reaction (12) (Fig. 2 and Table 1).

The XRD pattern of 1:1:1 mm′ – 117 Ht sample shows lines of major phases $BaCuO_2$, La_2O_3 and those of minor phase of La_2CuO_4 (Fig. 3b).

55.2% mass of residue observed at the end of TG at 1273 K (Table 1) corresponds to the sum of percentages of masses of La_2O_3, CuO and BaO and it is closest to the calculated percentage mass, 55.39. Therefore, reactions proposed in the decomposition processes in the case of 1:1:1 mm′ sample are found to be consistent with results obtained in TG and DTA and phases appeared in XRD patterns (Figs 1–3 and Table 1).

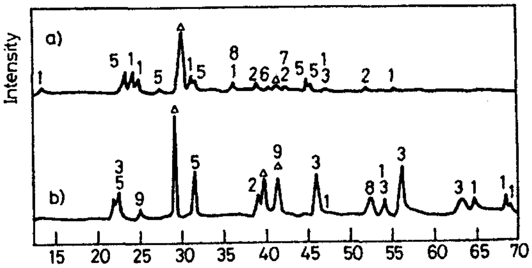

Fig. 3 XRD patterns of a) 1:1:1 mm′ — 8 Ht and b) 1:1:1 mm′ — 117 Ht samples
1) La_2CuO_4, 2) CuO, 3) La_2O_3, 4) BaO, 5) $La_2O_2CO_3/La_2CO_5$, 6) Cu, 7) BaO_2, 8) Cu_2O, 9) $BaCO_3$, Δ) $BaCuO_2$

In the case of 1:2:3 mm′ sample (Figs 1, 2 and 4 and Table 1):

In the step I from 313 to 513 K (Fig. 1 and Table 1) ~10.26% mass loss corresponds to the loss of $10H_2O$ species in the following endothermic reactions:

(i) starting with 3 mol of Cu(II) oxalate $3H_2O$ are lost in reaction (2) and

(ii) loss of $7H_2O$ species is accounted in the following reaction:

$$(La_2(C_2O_4)_3 \cdot 2BaC_2O_4) \cdot 7H_2O(s) \xrightarrow{\text{endothermic}}$$

$$La_2(C_2O_4)_3 \cdot 2BaC_2O_4(s) + 7H_2O(g) \qquad (13)$$

The endo-peak around 373 K observed on DTA trace of 1:2:3 mm′ (Fig. 2b) is assigned for reactions (2) (for 3 mol) and (13).

In the step II from 513 to 553 K (Fig. 1 and Table 1) ~14.535% mass loss corresponds to the loss of $6CO_2$ and uptake of $0.75O_2$ species in the exothermic reaction (3) for 3 mol of Cu(II) oxalate generating $1.5Cu_2O$ [4, 5]. The mass gain is observed at point Q on TG trace of 1:2:3 mm′ (Fig. 1).

The exo-peak ~553 K traced in DTA of 1:2:3 mm′ (Fig. 2b) is correlated with reaction (3) for 3 mol.

The XRD pattern of 1:2:3 mm′ – 5 Ht sample (Fig. 4a) shows lines of, Cu_2O and CuO and therefore upto 593 K there is no complete oxidation of copper.

In the step III from 553 to 653 K (Fig. 1 and Table 1) ~1.7% mass loss corresponds to the loss of CO species in the reaction (4) producing intermediate species Int′ in the decomposition of La(III) oxalate [6, 7].

In the step IV from 653 to 668 K (Fig. 1 and Table 1) ~6.84% mass loss corresponds to the loss of $2CO_2$ and CO species in the reaction (6) producing intermediate species Int″ in the decomposition of Int′ formed in reaction (4).

The exo-peak around 673 K on DTA trace (Fig. 2b) is assigned for reactions (5 and 6) (Table 1).

The XRD pattern of 1:2:3 mm′ – 6 Ht sample (Fig. 4b) shows lines of CuO only therefore it is concluded that upto 668 K 3Cu(II) oxalate are completely decomposed to 3CuO however, uptake of $0.75O_2$ is not recorded on TG trace.

In the step V from 668 to 793 K (Fig. 1 and Table 1) ~3.55% mass loss corresponds to the loss of 2CO species in the reaction (7) for 2 mol of Ba(II) oxalate producing $2BaCO_3$ [12, 13].

In the step VI from 793 to 1093 K (Fig. 1 and Table 1) ~3.56% mass loss corresponds to the loss of CO and $0.5CO_2$ species in the following reactions: (i) loss of CO species in the reaction (8) producing $La_2O_2CO_3$ while (ii) loss of $0.5CO_2$ in the decomposition of $0.5BaCO_3$ in the reaction (9) for 0.5 mol, generating 0.5BaO.

The exo-peak at ~773 K observed on DTA trace of 1:2:3 mm′ (Fig. 2b and Table 1) is assigned for reactions (7) for 2 mol and (8).

The XRD pattern of 1:2:3 mm′ – 8 Ht sample (Fig. 4c) shows lines of well developed phases of $La_2O_2CO_3$, CuO and those of minor phases Cu_2O and BaO.

Carbon dioxide generated in all the reactions upto 800 K occupies the space in the sample cell and therefore, the decomposition of mixture around 800 K will proceed in the presence of CO_2 gas. If it is assumed that some fraction of the total amount of carbon monoxide evolved in reactions (4) and (6) to (8) reduces CuO to Cu_2O about 800 K as follows:

$$2CuO(s) + CO(g) \xrightarrow{\text{endothermic}} Cu_2O(s) + CO_2(g) \tag{14}$$

the endo-peak around 816 K observed on DTA trace (Fig. 2b) is assigned for the reaction (14).

The decomposition of Ba(II) carbonate will take place at temperatures >873 K (step VI). The endo-peak at ~933 is allotted to reaction (9) for 0.5 mol (Fig. 2b and Table 1).

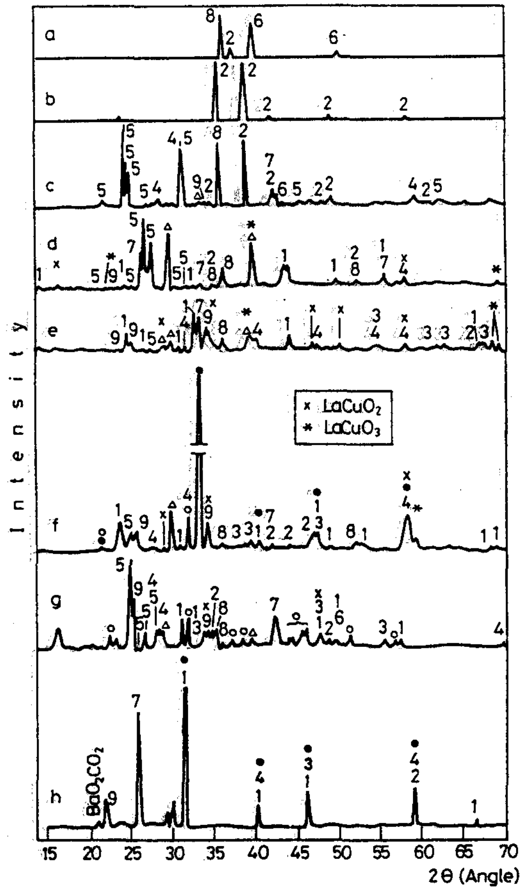

Fig. 4 XRD patterns of 1:2:3 mm' - samples: a) 5 Ht b) 6 Ht, c) 8 Ht, d) 10 Ht, e) 11 Ht, f) 116 Ht, g) 117 Ht, or h) 125 Ht; 1) La_2CuO_4, 2) CuO, 3) La_2O_3, 4) BaO, 5) $La_2O_2CO_3/La_2CO_5$, 6) Cu, 7) BaO_2, 8) Cu_2O, 9) $BaCO_3$, △) $BaCuO_2$, •) $La_{0.5}Ba_{0.5}CuO_{3-\delta}$ and o) $LaBa_2Cu_3O_{7-\delta}$ ($\delta'\to 0$)

0.5BaO reacts with 0.5CuO in the reaction (10) [17] and develops the phase $0.5BaCuO_2$ which appears predominantly in the XRD pattern of 1:2:3 mm' – 10 Ht sample (Fig. 4d). The endo-peak around 1068 K traced in DTA of 1:2:3 mm' (Fig. 2b and Table 1) is correlated with the reaction (10) for 0.5 mol. Thus, the residual products at the end of step VI are, $La_2O_2CO_3$, $1.5BaCO_3$, $0.5BaCuO_2$ and 2.5CuO. In this sample also, the temperature shift of $\Delta T \approx 400$ K is observed in the case of decomposition of $BaCO_3$ (see the discussion of step IV in TG of 1:1:1 mm').

In the step VII from 1093 to 1273 K (Fig. 1 and Table 1) ~5.32% mass loss corresponds to the loss of $2CO_2$ in the following reactions:

(i) in the reaction (11) producing La_2O_3 and
(ii) in the reaction (9) generating BaO.

The XRD pattern of 1:2:3 mm′ – 11 Ht sample (Fig. 4e) shows lines of various minor phases La_2O_3, $La_2O_2CO_3$, La_2CuO_4, $LaCuO_3$, $BaCO_3$, BaO, $BaCuO_2$ and CuO. It appears that as soon as La_2O_3 is produced (reaction (11)) CuO and BaO react with it and develop different phases [15, 17, 18] as follows:

(i) La_2CuO_4 in reaction (12), and

(ii) $$2La_2O_3(s) + 4BaO(s) + 8CuO(s) + O_2(g) \longrightarrow 8La_{0.5}Ba_{0.5}Cu^{II}O_{2.5}(s) \qquad (15)$$

In the present work, it is assumed that about $0.5La_2O_3$ reacts in reaction (12) and produce $0.5La_2CuO_4$ while remaining $0.5La_2O_3$ will react with BaO, 2CuO and $0.5O_2$ and develop the phase $2La_{0.5}Ba_{0.5}Cu^{II}O_{2.5}$ [18–21].

The endo-peak around 1136 K observed on DTA trace of 1:2:3 mm′ (Fig. 2b Table 1) is allotted to reactions (11), (12) and (15).

The XRD pattern of 1:2:3 mm– 116 Ht (Fig. 4f) shows lines of only one predominant phase of $La_{0.5}Ba_{0.5}CuO_{2.5}$ [18–21]. It is reported earlier [19] that in excess of BaO the development of the phase La_2CuO_4 is supressed and $La_{1-x}Ba_xCuO_{3-\delta}$ phase is produced for $x>0.2$.

As the intensity of lines of phases $La_{0.5}Ba_{0.5}CuO_{2.5}$ and $BaCuO_2$ decreases to a great extent and lines of new phase $LaBa_2Cu_3O_{7-\delta}$, orthorhombic phase ($\delta\rightarrow0$) [22] appear in the XRD pattern of 1:2:3 mm′ – 117 Ht sample (Fig. 4g) the following reaction is proposed:

$$2La_{0.5}Ba_{0.5}Cu^{II}O_{2.5}(s) + BaCuO_2(s) \xrightarrow{\text{endothermic}} LaBa_2Cu_3O_{7-\delta}\ (\delta\rightarrow0)(s) \qquad (16)$$

In the present work, $0.5BaCuO_2$ available at the end of step VI will react with $La_{0.5}Ba_{0.5}Cu^{II}O_{2.5}$ and produce $0.5LaBa_2Cu_3O_{7-\delta}$ ($\delta\rightarrow0$) in reaction (16).

The XRD pattern of 1:2:3 mm′ – 125 Ht (Fig. 4h) shows lines of phases $BaCO_3$, BaO_2, La_2CuO_4 and $La_{0.5}Ba_{0.5}Cu^{II}O_{2.5}$. It appears that at 1253 K small fraction of Ba(II) carbonate is decomposed to BaO_2 which appears in XRD pattern as follows:

$$BaCO_3 \xrightarrow{\text{endothermic}} BaO + CO_2 \qquad (9)$$

$$2BaO + O_2 \xrightarrow{\text{exothermic}} 2BaO_2(s) \qquad (17)$$

The endo-peak around 1213 K observed on DTA trace of 1:2:3 mm′ (Fig. 2b and Table 1) is correlated with reactions (16), (9) and (17).

At 1273 K, 55.945% mass of residue (Table 1) corresponds to the sum of percentages of masses of La_2O_3, 1.5BaO, $0.45BaCO_3$, $0.05BaO_2$ and 3CuO where calculated percentage mass of the above composition of residue is found to be 54.235. Therefore, reactions proposed in the case of 1:2:3 mm′ are consistent with results obtained in TG and DTA and phases appeared in XRD patterns (Figs 1–4 and Table 1).

Considering all the results shown in Figs 1–4, the reactivity of all the three oxalates in mixtures, under the present experimental set up is discussed below:

(A) Reactivity with respect to the decomposition of oxalates (Fig. 1 and Table 1):

(a) The decomposition of Cu(II) oxalate is affected only in 1:1:1 mm′ sample in which it starts at ~473 K in step II (Table 1) instead of 563 K [4, 5] to produce Cu(I) oxide (reaction (3)) and hence the temperature shift of $\Delta T \approx 80$ K towards lower temperature side.

(b) Decomposition of La(III) oxalate:

(i) The decomposition of La(III) oxalate to organic part (reaction (4)) is drastically affected in 1:1:1 mm′ sample. Instead of 653 K it starts around 523 K in step II in the case of 1:1:1 mm′ while at ~603 K in step III in the case of 1:2:3 mm′ [6, 7]. (Table 1) and hence the observed temperature shifts of $\Delta T_s \approx 100$ K and 50 K respectively towards lower temperature side.

(ii) The decomposition of Int″ (intermediate species formed in reaction (6)) to La(III) oxycarboníte (reaction (8)) in step IV in the case of 1:1:1 mm′ and in the step VI in the case of 1:2:3 mm′ remains unaffected and,

(iii) Decomposition of La(III) oxycarbonate to La(III) oxide (reaction (11)) in step V remains unaffected in the case of 1:1:1 mm′ while in the case of 1:2:3 mm′ sample it starts around 1093 K in step VII instead of 953 K and hence the temperature shift of $\Delta T \approx 150$ K towards higher temperature side.

(c) Decomposition of Ba(II) oxalate:

(i) Decomposition of Ba(II) oxalate to Ba(II) carbonate (reaction (7)) is affected only in 1:1:1 mm′ sample in which it starts around 630 K in step III (Table 1) instead of 768 K [12, 13] resulting in the temperature shift of $\Delta T \approx 125$ K towards lower temperature side and

(ii) Decomposition of Ba(II) carbonate to Ba(II) oxide.

Decomposition of Ba(II) carbonate to Ba(II) oxide (reaction (9)) starts in step IV in 1:1:1 mm′ and in step VI in 1:2:3 mm′ around 820 K instead of ≈1273 K [14] and therefore temperature shift of $\Delta T \approx 400$ K is observed in both the cases (Table 1).

Some amounts of CO and CO_2 gases evolved in reactions (4) and (6) to (8) prevent the oxidation of Ba(II) oxide. The small crystalline particles of oxide are trapped in the sample during cooling from 873 K to room temperature and corresponding lines appear in XRD patterns of 1:1:1 and 1:2:3 mm′ – 8 Ht samples (Fig. 3a and Fig. 4c).

No complete decomposition occurs in the case of 1:2:3 mm′ sample as $1.5BaCO_3$ decomposes in the steps VI and VII and $0.45BaCO_3$ remains in the residue at the TG end at 1273 K (Table 1).

Therefore, with respect to the decomposition of oxalates the reactivity is higher in 1:1:1 mm′ sample.

(B) Reactivity with respect to the formation of various cuprate compounds.

The appearance of 4 and 6 endo-peaks on DTA traces of 1:1:1 and 1:2:3 mm′ samples (Fig. 2) respectively indicates that there exists reactions amongst the decomposition products to provide new phases and indeed phases of La_2CuO_4 and $BaCuO_2$ (reactions (10) and (12)). i.e., reactive combinations of CuO with La_2O_3 or BaO, arrive in XRD patterns of 1:1:1 and 1.2.3 mm′ (Fig. 3b and Fig. 4d–h) while lines of $La_{0.5}Ba_{0.5}CuO_{3-\delta}$ ($\delta \to 0.5$) (reaction (15)) and lines of $LaBa_2Cu_3O_{7-\delta}$ ($\delta \to 0$) phases [18, 22] (reaction (16)) appear in XRD patterns of 1:2:3 mm′ – 116 Ht and 117 Ht samples (Fig. 4f and g) respectively.

The disappearance of the phase $LaBa_2Cu_3O_{7-\delta}$ ($\delta \to 0$) in XRD pattern of 1:2:3 mm′ – 125 Ht sample (Fig. 4h) indicates that the phase is decomposed in the reverse reaction (16) as $La_{0.5}Ba_{0.5}CuO_{3-\delta}$ ($\delta \to 0.5$) appears predominantly in 125 Ht sample (Fig. 4h).

At 1173 K the mixture 1:1:1 mm′ will provide a composite of Ba(II) cuprate and small amount of La(III) cuprate while 1:2:3 mm′ will provide composite of $La_{0.5}Ba_{0.5}CuO_{3-\delta}$ ($\delta \to 0.5$) [18] and $LaBa_2Cu_3O_{7-\delta}$ ($\delta \to 0$) [22] phases along with small amounts of cuprates of La(III) and Ba(II) and Ba(II) carbonate i.e. a composite of metallic and superconducting phases along with impurities of carbonates.

Therefore, with respect to the formation of various mixed cuprate phases having characteristic properties the reactivity of 1:2:3 mm′ mixture is higher than that of 1:1:1 mm′ sample.

* * *

Authors are deeply thankful to the Authorities of Department of Atomic Energy (DAE), Goverment of India, for providing the funds for research project and to Professor A. V. Phadke, Department of Geology, University of Poona, for the valuable discussion.

References

1 C. N. R. Rao and J. Gopalakrishnan, 'New directions in solid state chemistry', Cambridge Solid State Science Series. Cambridge University press, New York, Sydney. 1989, Chapter 9 p. 488.
2 T. V. Ramakrishnan and C. N. R. Rao, 'Superconductivity Today', Wiley Eastern Ltd., New Delhi, Bangalore, 1992, Chapter 3 pp. 47–48.
3 D. Dollimore, Thermochim. Acta, 117 (1987) 335.
4 D. Broadbent, J. Dollimore, T. A. Evans and D. Dollimore, JCS Faraday Trans., 87 (1991) 161.
5 A. Coetzee, D. J. Eve and M. E. Brown, J. Thermal Anal., 39 (1993) 947.
6 K. G. Nair, V. V. Sreerajan, V. S. V. Nayar and C. G. R. Nair, Thermochim. Acta, 39 (1980) 256.
7 R. Möbius, W. Dietzold and F. Matthes, J. Inorg. Nucl. Chem., 28 (1966) 1848, 1852.
8 Y. Saito and S. Sasaki, Netsusoketei, 7 (1980) 67.
9 P. K. Gallagher and F. Schrey, Thermochim Acta, 1 (1970) 465.
10 O. K. Shirvastava and A. R. Vasudeva Murthy, J. Sci., Ind. Res. India, 21B (1962) 525.
11 D. Dollimore, ibid, 334.
12 D. Dollimore and D. V. Nowellin Thermal Analysis, Proc., 4th ICTA, Vol. 3, (Ed. I. Buzás) Académiai Kiadó, Budapest 1975, p. 63.

13 D. Dollimore and D. L. Griffiths, J. Thermal Anal., 2 (1970) 229.
14 R. Rauch and E. Kaisersberger, Proc. Seventh Nat. Symp. on Thermal Anal. held at Shrinagar, India 1989, p. 6.
15 C. N. R. Rao and J. Gopalakrishnan, ibid p. 488.
16 ibid p. 477.
17 H. N. Migeon, F. Jeannot, M. Zanne and J. P. Aubry, Rev. Chim. Miner, 13 (1976) 440.
18 A. Dwivedi, M. A. Rodriguez and A. N. Cormack, J. Am. Ceram. Soc., 75 (1992) 1993.
19 ibid 1994.
20 ibid 1994, 1995.
21 L. Er-Rakho, C. Michel, J. Provost and B. Raveau, J. Solid State Chem.,, 37 (1981) 151.
22 L. Ganapathi, A. K. Ganguli, R. A. Mohanram and C. N. R. Rao, J. Solid State Chem., 73 (1988) 593.
23 C. N. R. Rao and J. Gopalakrishnan, ibid – Chapter 9 (1989) pp. 483, 485.
24 D. Dollimore, D. L. Griffiths and D. Nicholson, J. Chem. Soc., (1962) 960.
25 C. H. Bamford and C. F. H. Tipper 'Comprehensive chemical kinetics', Elsevier Science Publishers, Elsevier, North Holland, Excerpta Medica, 22 (1980) 218.
26 C. N. R. Rao and J. Gopalakrishnan, ibid, Chapter 9 (1989) 476, 477.