Journal of Thermal Analysis and Calorimetry, Vol. 62 (2000) 285–294

REACTIVITY OF BINARY MIXTURES OF La(III) OXIDE AND Cu(II) OXALATE OR NITRATE AND SYNTHESIS OF La(III) CUPRATE

L. Bapat[1], *G. N. Natu*[2], *J. Kher*[1] *and M. Bhide*[1]

[1]Department of Chemistry, N. Wadia College, Pune 411 001
[2]Department of Chemistry, University of Pune, Pune 411 007, India

(Received February 10, 1999; in revised form December 30, 1999)

Abstract

Reactivity of mixtures of La(III) oxide and Cu(II) oxalate/nitrate in hydrated as well as anhydrous state was studied using TG, DTA and XRD.

Cu(II) oxide formed in the endothermic decomposition of mixture containing hydrated Cu(II) nitrate and La(III) oxide could not form La_2CuO_4 while Cu(II) oxide formed in the exothermic decomposition of mixture containing hydrated/anhydrous Cu(II) oxalate and La(III) oxide reacts with La(III) oxide and develops the phases $CuLaO_3$ and La_2CuO_4.

The maximum reactivity with respect to the formation of La_2CuO_4 phase was observed in mixture containing anhydrous Cu(II) oxalate.

Keywords: reactivity of La_2O_3, synthesis of La_2CuO_4, thermal decomposition of La_2O_3 and CuC_2O_4 or $Cu(NO_3)_2$

Introduction

La(III) cuprate containing excess oxygen [1, 2] or alkaline earth metal ions substituted at sites of La(III) ions [3–5] exhibits superconductivity at temperatures below 38 K. The superconducting ceramics are synthesized adopting different thermal procedures, (i) by firing and sintering corresponding oxides [6, 7] and (ii) by decomposing the mixtures of hydroxides, nitrates, carbonates, formates, citrates or oxalates of the corresponding cations, in appropriate proportions and sintering the oxide products at ~1273 K [1, 8, 9]. In these processes, attempts have been made to make a mixture of oxides in situ so that at lower sintering temperature the required compound can be formed in the single phase.

In the present work the synthesis of La(III) cuprate (La_2CuO_4 phase) is attempted by decomposing mixtures of La(III) oxide and Cu(II) oxalate/nitrate in hydrated as well as anhydrous state, at various temperatures in air and under reduced pressure. As Cu(II) nitrate/oxalate decomposes to Cu(II) oxide around 823 K [10–15] a homogeneous mixture of La(III) oxide and Cu(II) oxide will be formed and it is ex-

1418–2874/2000/ $ 5.00

Akadémiai Kiadó, Budapest
Kluwer Academic Publishers, Dordrecht

pected that there will be reaction between two oxides to form La_2CuO_4 phase at temperature below 1273 K.

Experimental

Pure crystalline monohydrate Cu(II) oxalate was prepared by mixing aqueous solutions of Cu(II) nitrate (Analar) and sodium oxalate (BDH). The following mixtures in 1:1 molar proportion were prepared by mechanical mixing of the appropriate quantities of dried La(III) oxide (E-Merck) with: (A) hexahydrate Cu(II) nitrate, (B) monohydrate Cu(II) oxalate and (C) anhydrous Cu(II) oxalate (prepared by degassing under vacuum at 423 K).

As hexahydrate Cu(II) nitrate decomposes to basic Cu(II) nitrate $Cu(NO_3)_2 \cdot 2Cu(OH)_2$ [10–13] during dehydration process it was not possible to prepare a mixture of pure anhydrous Cu(II) nitrate and La(III) oxide.

TG and DTA

TG and DTA traces of mixtures A and B were recorded in dry air at the heating rate 10 K min^{-1} in the temperature range of 298 to 1273 K on MOM Derivatograph OD type 102, using 200 mg mixture, α-Al_2O_3 as a reference material and platinum crucibles. Results are shown in Figs 1 and 3 and tabulated in Table 1.

Mixtures were heated at the rate 10 K min^{-1} upto 673, 823, 923, 1023, 1173 or 1223 K for 1 h (designated as 6Ht, 8Ht, 9Ht, 10Ht, 11Ht or 12Ht respectively) either in dry air or under reduced pressure ($1.0 \cdot 10^{-3}$ torr), rapidly cooled to room temperature and their X-ray powder diffraction (XRD) patterns were recorded on Rigaku PR-511 using

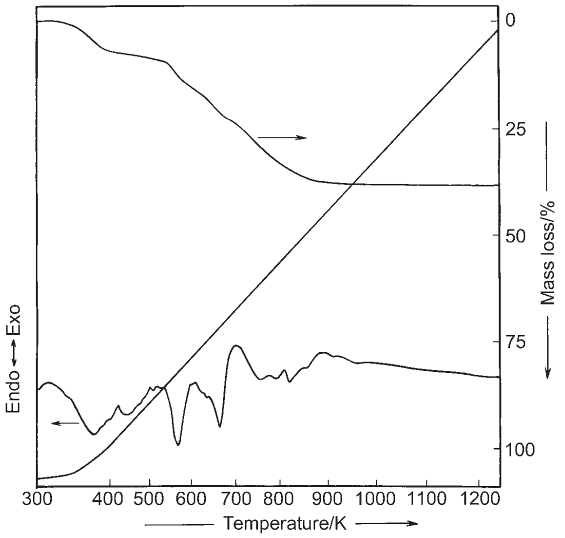

Fig. 1 TG-DTA traces of the mixture A

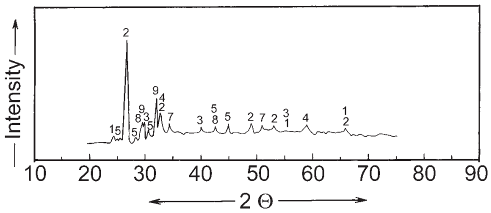

Fig. 2 XRD pattern of the sample A-12Ht

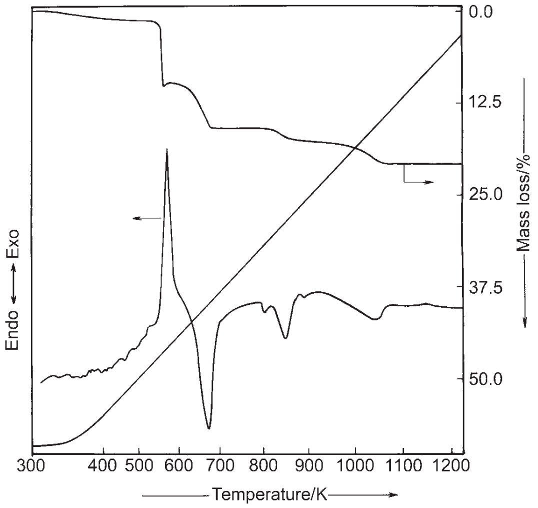

Fig. 3 TG-DTA traces of the mixture B

CuK$_\alpha$ radiation which are shown in Figs 2 and 4–7. Sample A-6Ht and A-V-6Ht represent mixture A heated at 673 K for 1 h, in air and under reduced pressure respectively.

Results and discussion

TG and DTA traces of mixture A (Fig. 1 and Table 1) reveal the following reactions (Table 2) [10–15, 19]:

(i) decomposition of hexahydrate Cu(II) nitrate to trihydrate and water (reaction (1)) and subsequent reaction of water with La(III) oxide (reaction (2)), resulting in the formation of La(III) hydroxide, (ii) decomposition of trihydrate to anhydrous Cu(II) nitrate and its further decomposition to Cu(II) oxide, oxygen and NO_2 gases (reactions (3) and (5)) and (iii) decomposition of La(III) hydroxide to La(III) oxide (reactions (4) and (7)).

Around 853 K mixture A decomposes to oxides of Cu(II) and La(III). Except the exothermic (exo-) reaction (2) all the rest of reactions are endothermic (endo-). As La(III)

Table 1 Thermal analysis data of decomposition of binary mixtures of (A) $Cu(NO_3)_2\cdot 6H_2O$+La_2O_3 and (B) $CuC_2O_4\cdot H_2O$+La_2O_3

Composition of mixture*	TG					DTA		
	T_{step}/K	Mass loss/%		mol**	Composition***	$Peak_{endo}$/K	$Peak_{exo}$/K	Reactions correlated
		obs.	theor					
$Cu(NO_3)2\cdot 6H_2O$+ La_2O_3	Step-I 298–533	10.2	8.7	–$3H_2O$	Anhydrous $Cu(NO_3)_2$, $2La(OH)_3$	~363 ~453	~313	(1), (2), (3)
	Step-II 533–793	23.3	23.22	–H_2O –$2HNO_3$	2LaO(OH), CuO	~573 ~643 ~663		(4) (5) (6)
	Step-III 793–1003	5.11	5.8	–$2H_2O$	La_2O_3, CuO	~753 broad ~823 broad		(7) (7)
	Total loss	38.61	37.72					

Table 1 Continued

Composition of mixture*	TG					DTA		
	T_{step}/K	Mass loss/% obs.	Mass loss/% theor.	mol**	Composition***	$Peak_{endo}$/K	$Peak_{exo}$/K	Reactions correlated
$CuC_2O_4 \cdot H_2O$ $+La_2O_3$ 1:1	Step-I 303–533	1.22	0.91	$-0.25H_2O$	Anhydrous CuC_2O_4, $0.75La_2O_3$, $0.5La(OH)_3$ CuO		~313	(8), (2)
	Step-II 533–593	8.58	7.88	$-1.25CO_2$ $+0.5O_2$	$0.75La_2O_2CO_3$, $0.5La(OH)_3$ CuO		~568	(10) (9)
	Step-III 593–683	6.1	5.35	$-0.5CO_2$ $-0.25H_2O$	$0.25La_2(OH)_4CO_3$, $0.75La_2O_3$	~673		(4), (11), (12)
	Step-IV and Step-V	4.9	4.04	$-0.25CO_2$ $-0.5H_2O$	La_2O_3, CuO	~803 ~848 ~883 ~1043		(12), (13)
	793–893 893–1093						~1143	$CuLaO_3$ [20]
	Total loss	20.80	18.18					

[*] Mole proportion 1:1

[**] Loss (–) and uptake (+) of species, mol

[***] Composition at step end

Table 2 Reactions involved in the thermal decomposition of mixtures A, B and C

Reactions				References
$Cu(NO_3)_2 \cdot 6H_2O$	endothermic	$Cu(NO_3)_2 \cdot 3H_2O+3H_2O$	(1)	[10]
$La_2O_3+3H_2O$	exothermic	$2La(OH)_3$	(2)	[19]
$Cu(NO_3)_2 \cdot 3H_2O$	endothermic	$Cu(NO_3)_2+3H_2O$	(3)	[12, 13]
$La(OH)_3$	endothermic	$LaO(OH)+H_2O$	(4)	[19]
$2Cu(NO_3)_2$	endothermic	$2CuO+4NO_2+O_2$	(5)	[11, 12]
$4NO_2+O_2+2H_2O$		$4HNO_3$	(6)	
$2LaO(OH)$	endothermic	$La_2O_3+H_2O$	(7)	[19]
$CuC_2O_4H_2O$	endothermic	$CuC_2O_4+H_2O$	(8)	
$2CuC_2O_4+O_2$	exothermic	$2CuO+4CO_2$	(9)	[14, 15]
$La_2O_3+CO_2$	exothermic	$La_2O_2CO_3$	(10)	[20]
$La(OH)_3+LaO(OH)+CO_2$		$La_2(OH)_4CO_3$	(11)	[19]
$La_2O_2CO_3$	endothermic	$La_2O_3+CO_2$	(12)	[19]
$La_2(OH)_4CO_3$	endothermic	$La_2O_2CO_3+2H_2O$	(13)	[19]
$CuO+La_2O_3$	endothermic	La_2CuO_4	(14)	[1, 23]

lines of predominant phase of CuO. Therefore, oxides of Cu(II) and La(III) do not react.

The thermal analysis of mixture B (Fig. 3 and Table 1) reveals the following reactions (Table 2):

(i) dehydration of Cu(II) oxalate (reaction (8)) and reaction of evolved water with 0.25 moles of La(III) oxide to produce 0.5 moles of La(III) hydroxide (reaction (2)), (ii) at 568 K exothermic decomposition of Cu(II) oxalate to Cu(II) oxide and CO_2 gas (reaction (9)) and carbonation of the remaining 0.75 moles of La(III) oxide (reaction (10)) [17] to form 0.75 moles of $La_2O_2CO_3$ phase, (iii) at ~673 K decomposition of La(III) oxycarbonate to La(III) oxide (reaction (12)) and carbonation of La(III) hydroxide to yield $La_2(OH)_4CO_3$ compound (reactions (4) and (11)), (iv) at 1093 K complete decomposition of $La_2(OH)_4CO_3$ in reactions (13) and (12) to La(III) oxide and (v) around 1143 K reaction between oxides of Cu(II) and La(III) to develop the phase $CuLaO_3$ [21].

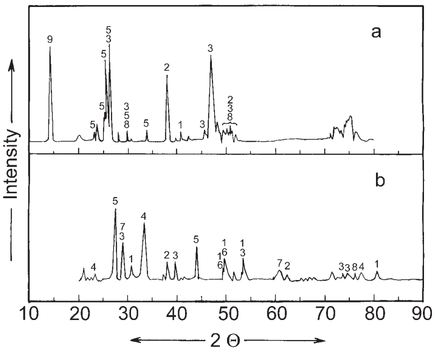

Fig. 4 XRD patterns of samples a – B-6Ht and b – B-11Ht

XRD pattern of B-6Ht sample (Fig. 4a) shows lines of CuO, Cu_2O, $La_2O_2CO_3$ and $La(OH)_3$ phases while that of B-11Ht sample (Fig. 4b) reveals lines of $CuLaO_3$ phase along with phases of unreacted oxides and lines of $CuLaO_2$ phase [22] with weak intensities.

It is found that although CuO phase appears at ~568 K (reaction (9)) La(III) oxide is not available free to react with it as during carbonation the phase of La(III) oxide is completely used up (reaction (10)) (Fig. 4a). On further heating at 1143 K both the oxides partially react to develop the phase $CuLaO_3$ (Fig. 4b) and probably the phase La_2CuO_4 will be developed at temperature greater than 1273 K. It appears that the presence of decomposition products CO_2 gas and water vapours (reactions (4), (8), (9), (12) and (13)) in between the surfaces of both the oxide particles, hinders the formation of La_2CuO_4 phase (reaction (14)). If it is assumed that CO_2 gas and water vapours are expelled out during heating of mixture B under reduced pressure (1.0×10^{-3} torr) there will be predominant phase formation of La_2CuO_4. On the contrary XRD patterns of B-V-6Ht and B-V-11Ht samples (Fig. 5a and b) show lines of $La(OH)_3$, $La_2O_2CO_3$ and CuO phases and those of weak intensities of La_2CuO_4 [1, 23].

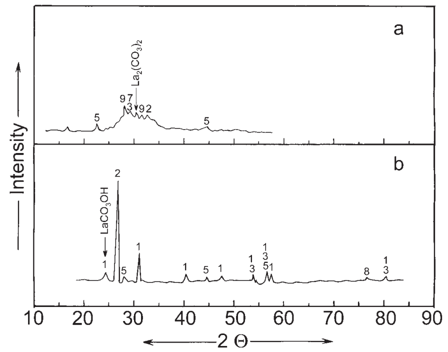

Fig. 5 XRD patterns of samples a – B-V-6Ht and b – B-V-11Ht

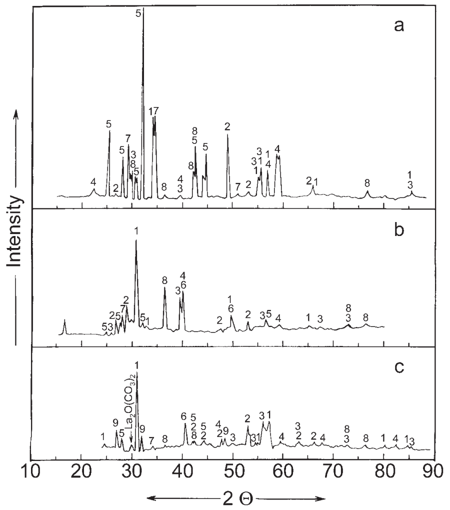

Fig. 6 XRD patterns of samples a – C-8Ht, b – C-9Ht and c – C-10Ht

As the XRD pattern of C-8Ht sample (Fig. 6a) shows lines of $La_2O_2CO_3$, CuO and $CuLaO_2$ phases it appears that there is carbonation of La(III) oxide with CO_2 gas evolved in the decomposition of anhydrous Cu(II) oxalate (reaction (9)) and hence at ~823 K no reaction of Cu(II) oxide with La(III) oxide is observed. On further heating oxycarbonate will decompose to La(III) oxide (reaction (12)) which will react with Cu(II) oxide and develop the phase La_2CuO_4 and indeed XRD pattern of C-9Ht sample (Fig. 6b) shows lines of well developed phase of La_2CuO_4 and other compounds viz. Cu_2O [14, 15] and La_2O_3 while pattern of C-10Ht exhibits lines of single phase of La_2CuO_4 (Fig. 6c). It is observed that the temperature at which La_2CuO_4 phase forms in the previous sintering processes [6, 7] is shifted by 250 K towards lower temperature side in the case of mixture C, i.e. from 1273 to 1023 K.

In order to avoid carbonation, the mixture C was heated under reduced pressure (1.0×10^{-3} torr) and it was expected that the phase La_2CuO_4 will form at ~823 K. On

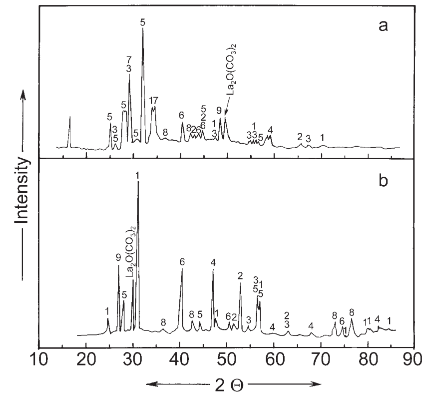

Fig. 7 XRD patterns of samples a – C-V-10Ht and b – C-V-12Ht

the contrary the XRD pattern of C-V-10Ht sample (Fig. 7a) shows lines of predominant phase $La_2O_2CO_3$. Therefore, it can be visualized that the carbonation occurs immediately after decomposition of Cu(II) oxalate to form $La_2O_2CO_3$ phase which is not decomposing upto ~1023 K. As the XRD pattern of C-V-12Ht sample (Fig. 7b) shows lines of La_2CuO_4, $CuLaO_3$ and Cu phases the thermal treatment of mixture C under reduced pressure is not useful to obtain single phase of La_2CuO_4.

It was found that while cooling unreacted La(III) oxide reacts with residual moisture and CO_2 gas present in the reaction cell in all mixtures and forms La(III) hydroxide and La(III) oxycarbonate [19, 20] in trace amounts as seen in Figs 2, 4b, 5b, 6c and 7b.

Considering all the results shown in Figs 1–7 and tabulated in Table 1 it can be concluded that the mixture of anhydrous Cu(II) oxalate and dried La(II) oxide shows highest reactivity with respect to the formation of La_2CuO_4 phase.

* * *

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

References

1 C. N. R. Rao and J. Gopalakrishnan, ‘New directions in solid state chemistry’, Chapter 9, Cambridge Solid State Science Series, Cambridge University Press, Cambridge, New York 1989, pp. 476, 488, 489.
2 K. Sekizwa, Y. Takano, H. Takigami, S. Tasaki and T. Inaba, Jpn. J. Appl. Phys., 26 (1987) L840.
3 C. Politis, J. Geerk, M. Dietrich and B. Obst, Z. Phys. B-Condensed Matter, 64 (1986) 189.
4 R. J. Cava, R. B. Van Dover, B. Batlogg and E. A. Rietman, Phys. Rev. Lett., 58 (1987) 408.
5 H. Takagi, S. Uchida, K. Kitazawa and S. Tanaka, Jpn. J. App. Phys., 26 (1987) L123.
6 T. Arakwa, G. Adachi and J. Shiokawa, Nippon Kagaku Kaishi, 10 (1980) 1573.

7 J. C. Park, P. V. Huong, M. Rey-Lafon, J. C. Grenier, A. Wattiaux and M. Pouchard, Physica C, 177 (1991) 487.

8 T. V. Ramakrishnan and C. N. R. Rao, ‘Superconductivity today’, Chapter 3, Wiley Eastern Ltd., New Delhi 1992, pp. 47, 48.

9 V. F. Savchenko and Ya. S. Rubinchik, Izu. Akad. Nauk SSSR, Neorg. Mater., 13 (1977) 2038.

10 T. J. Taylor, D. Dollimore and G. A. Gamlen, Thermochim. Acta., 103 (1986) 333, 334 and 340.

11 S. Peltier and C. Duval, Compt. Rend., 226 (1948) 1727.

12 E. D. Pierron, J. A. Rashkin and J. F. Roth, J. Catal., 9 (1967) 38.

13 S. Gordon and C. Campbell, Anal. Chem., 27 (1955) 1102.

14 D. Broadbent, J. Dollimore, T. A. Evans and D. Dollimore, JCS Faraday Trans., 87 (1991) 161.

15 A. Coetzee, D. J. Eve and M. E. Brown, J. Thermal Anal., 39 (1993) pp. 953.

16 S. A. A. Mansour, J. Thermal Anal., 46 (1996) 263.

17 B. R. Carson, G. Kenessey, J. R. Allan and G. Liptay, J. Thermal Anal., 45 (1995) 369 and 46 (1996) 1577.

18 M. A. A. Elmasry, A. Gaber and E. M. H. Khater, J. Thermal Anal., 47 (1996) 757.

19 S. Bernal, F. J. Botana, R. Garcia and J. M. Rodriguez-Izquierdo, Thermochim. Acta, 66 (1983) 142, 143, 145.

20 O. A. Songina, ‘Rare Metals (Redkie Metally)’ Chapter 6, 3rd Ed. Israel Program for Scientific Translations Ltd. Jerusalem, 1970 translated (to English) by J. Schmorak, Keter Press, Jerusalem. 1970, p. 180.

21 A. Dwivedi, M. A. Rodriguez and A. N. Cormack, J. Am. Ceram. Soc., 75 (1993) 1993.

22 H. Haas and E. Kordes, Z. Kristallogr., 129 (1969) 259.

23 L. Lehvede and M. Daire, C. R. Acad. Sci. Ser. C, 276 (1973) 1011.

24 R. G. Rupard and P. K. Gallagher, Thermochim. Acta, 272 (1996) 11.

25 A. M. Mansour Donia and D. Dollimore, Thermochim. Acta, 290 (1997) 139.

26 A. M. Donia, Polyhedron, 16 (1999) 3013.